Supplementary Information for

Bis(2-quinolylmethyl)ethylenediaminediacetic acids (BQENDAs), TQEN-EDTA hybrid molecules as fluorescent zinc sensors

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Experimental

***N,N*-Bis(2-quinolylmethyl)-*N'*-(*tert*-butoxycarbonyl)ethylenediamine (3a).** To the dry CH_3CN solution (50 mL) of 2-chloromethylquinoline (470 mg, 2.65 mmol) and *N*-Boc-ethylenediamine (212 mg, 1.32 mmol) was added potassium carbonate (1.10 g, 8.0 mmol) and potassium iodide (660 mg, 3.98 mmol), then refluxed for 2 days under N_2. The resultant solution was cooled to r.t. and the solvent was evaporated. After addition of $CHCl_3$, the precipitate was filtered and the filtrate was evaporated to give compound **3a** as a brown oil (581 mg, 1.31 mmol, 99%). ^{1}H NMR ($CDCl_3$): δ 8.17 (d, *J* = 8.9 Hz, 2 H), 8.07 (d, *J* = 8.2 Hz, 2 H), 7.77 (d, *J* = 8.1 Hz, 2 H), 7.69 (dd, *J* = 8.5, 6.7 Hz, 2 H), 7.55 (d, *J* = 8.5 Hz, 2 H), 7.50 (ddd, *J* = 7.9, 7.9, 0.9 Hz, 2 H), 6.60 (br., 1 H), 4.09 (s, 4 H), 3.321 (m, 2 H), 2.85 (m, 2 H), 1.51 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 159.7, 147.4, 136.3, 129.3, 129.0, 127.4, 127.3, 126.2, 121.0, 61.0, 53.7, 39.1, 28.9. Anal Calcd. for $C_{27}H_{30}N_4O_2$ (**3a**): H, 6.83; C, 73.28; N, 12.66. Found: H, 7.00; C, 73.54; N, 12.75.

***N,N*-Bis(1-isoquinolylmethyl)-*N'*-(*tert*-butoxycarbonyl)ethylenediamine (3b).** To the dry CH_3CN solution (100 mL) of 1-chloromethylisoquinoline (907 mg, 5.10 mmol) and *N*-Boc-ethylenediamine (409 mg, 2.55 mmol) was added potassium carbonate (2.80 g, 20.3 mmol) and potassium iodide (1.70 g, 10.2 mmol), then refluxed for 2 days under N_2. The resultant solution was cooled to r.t. and the solvent was evaporated. After addition of $CHCl_3$, the precipitate was filtered and the filtrate was evaporated to give compound **3b** as a brown oil (quant.). ^{1}H NMR ($CDCl_3$): δ 8.43 (d, *J* = 5.8 Hz, 2 H), 8.04 (d, *J* = 9.2 Hz, 2 H), 7.77, (d, *J* = 8.9 Hz, 2 H), 7.61 (dd, *J* = 7.9, 7.0 Hz, 2 H), 7.54 (d, *J* = 6.1 Hz, 2 H), 7.33 (dd, *J* = 7.9, 7.0 Hz, 2 H), 5.77 (br., 1 H), 4.37 (s, 4 H), 3.25 (br., 2 H), 2.84 (dd, *J* = 6.4, 5.5 Hz, 2 H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.7, 141.2, 136.0, 129.7, 127.1, 126.9, 126.7, 125.7, 120.4, 59.4, 53.9, 38.4, 28.6. Anal Calcd. for $C_{27.5}H_{31.5}Cl_{1.5}N_4O_{2.5}$ (**3b**): H, 6.83; C, 73.28; N, 12.66. Found: H, 7.03; C, 73.14; N, 12.94.

***N,N*-Bis(2-quinolylmethyl)ethylenediamine (4a).** Compound **3a** (581 mg, 1.31 mmol) was dissolved in conc. HCl (5.0 mL) and stirred overnight at r.t. Aqueous NaOH solution (5*N*) was added until pH 11 and the solution was extracted with CH_2Cl_2. The organic layer was dried, evaporated and washed with CH_3CN to give compound **4a** as a white powder (417 mg, 1.22 mmol, 93%). ^{1}H NMR ($CDCl_3$): δ 8.13 (d, *J* = 8.5 Hz, 2 H), 8.05 (d, *J* = 8.5 Hz, 2 H), 7.78 (d, *J* = 8.5 Hz, 2 H), 7.66-7.72 (m, 4 H), 7.50 (ddd, *J* = 8.2, 7.9, 1.2 Hz, 2 H), 4.05 (s, 4 H), 2.80 (br., 2 H), 2.75 (br., 2 H). ^{13}C NMR ($CDCl_3$): δ 160.1, 147.5, 136.3, 129.4, 129.0, 127.5, 127.3, 126.2, 121.0, 62.0, 58.2, 40.0. Anal Calcd. for $C_{22}H_{22.9}N_4O_{0.45}$ (**4a**): H, 6.48; C, 77.16; N, 16.36. Found: H, 6.28; C, 77.32; N, 16.11.

***N,N*-Bis(1-isoquinolylmethyl)ethylenediamine (4b).** Compound **3b** (1.20 g, 2.60 mmol) was dissolved in conc. HCl (10.0 mL) and stirred overnight at r.t. Aqueous NaOH solution (5*N*) was added until pH 11 and the solution was extracted with $CHCl_3$. The organic layer was dried, evaporated and washed with CH_3CN to give compound **4b** as a cream-colored powder (829 mg, 2.42 mmol, 93%). ^{1}H NMR ($CDCl_3$): δ 8.43 (d, *J* = 5.8 Hz, 2 H), 7.97 (d, *J* = 8.5 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 7.59 (ddd, 7.0, 7.0, 1.2 Hz, 2 H), 7.56 (d, *J* = 6.4 Hz, 2 H), 7.22-7.28 (m, 2 H), 4.32 (s, 4 H), 2.77 (dd, 3.1, 2.4 Hz, 4 H). ^{13}C NMR ($CDCl_3$): δ 158.2, 141.4, 136.2, 129.8, 127.5, 127.0, 126.7, 120.7, 60.5, 58.1, 39.7. Anal Calcd. for $C_{22.2}H_{22.6}Cl_{0.6}N_4O_{0.2}$ (**4b**): H, 6.48; C, 77.16; N, 16.36. Found: H, 6.33; C, 76.98; N, 16.28.

***N,N*-Bis(2-quinolylmethyl)-*N',N'*-bis(*tert*-butoxycarbonylmethyl)ethylenediamine (5a).** To the DMF solution (3 mL) of compound **4a** (200 mg, 0.58 mmol) and *tert*-butyl bromoacetate (0.17 mL, 1.16 mmol) was added potassium carbonate (660 mg, 4.76 mmol) and potassium iodide (400 mg, 2.40 mmol), then stirred for 4 days at r.t. under N_2. After addition of water, the reaction mixture was extracted with $CHCl_3$ and the organic layer was washed with brine, dried, evaporated and washed with CH_3CN to give compound **5a** as a light yellow powder (275 mg, 0.48 mmol, 83%). ^{1}H NMR ($CDCl_3$): δ 8.10 (d, *J* = 8.5 Hz, 2

H), 8.03 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 7.71 (d, *J* = 8.1 Hz, 2 H), 7.66 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 2 H), 7.49 (ddd, *J* = 8.1, 6.9, 1.2 Hz 2 H), 4.05 (s, 4H), 3.39 (s, 4 H), 2.99 (dd, *J* = 7.6, 6.0 Hz, 2 H), 2.79 (dd, *J* = 7.6, 6.0, 2 H), 1.35 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 170.4, 160.4, 147.4, 136.2, 129.2, 129.0, 127.4, 127.3, 126.0, 121.2, 80.9, 61.7, 56.2, 53.0, 52.1. Anal Calcd. for $C_{34}H_{43}N_4O_{4.5}$ (**5a**·0.5H_2O): H, 7.48; C, 70.44; N, 9.66. Found: H, 7.30; C, 70.42; N, 9.61.

***N,N*-Bis(1-isoquinolylmethyl)-*N',N'*-bis(*tert*-butoxycarbonylmethyl)ethylenediamine (5b).** To the DMF solution (3 mL) of compound **4b** (653 mg, 1.91 mmol) and *tert*-butyl bromoacetate (0.56 mL, 3.82 mmol) was added potassium carbonate (2.20 g, 16.0 mmol) and potassium iodide (1.30 g, 7.83 mmol), then stirred for 4 days at r.t. under N_2. After addition of water, the reaction mixture was extracted with $CHCl_3$ and the organic layer was washed with brine, dried, evaporated and washed with CH_3CN to give compound **5b** as a white powder (930 mg, 1.60 mmol, 84%). ^{1}H NMR ($CDCl_3$): δ 8.42 (d, *J* = 6.0 Hz, 2 H), 8.15 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H), 7.59 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2 H), 7.54 (d, *J* = 6.4 Hz, 2 H), 7.20 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2 H), 4.28 (s, 4 H), 3.26 (s, 4 H), 2.98 (dd, *J* = 6.7, 6.7 Hz, 2 H), 2.73 (dd, *J* = 6.7, 6.7 Hz, 2 H), 1.32 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 170.2, 158.5, 141.3, 136.2, 129.8, 127.6, 127.3, 126.5, 126.54, 120.48, 80.7, 60.4, 55.4, 52.5, 50.5. Anal Calcd. for $C_{34}H_{42}N_4O_4$ (**5b**): H, 7.42; C, 71.55; N, 9.82. Found: H, 7.50; C, 71.39; N, 9.77.

***N,N'*-Bis(2-quinolylmethyl)ethylenediamine (6a).**[1] To the MeOH solution (30 mL) of quinoline-2-carboxaldehyde (230 mg, 1.4 mmol) was added ethylenediamine (0.05 mL, 0.7 mmol) in MeOH solution (7 mL) at 0 °C, and stirred for 1.5 h at r.t. After evaporation of the solvent, the residue was dissolved in EtOH (25 mL) and $NaBH_4$ (150 mg, 4.0 mmol) was added, then stirred overnight at r.t. After evaporation of the solvent, water was added and the

product was extracted with $CHCl_3$. The organic layer was dried and evaporated to give compound **6a** as a colorless oil (230 mg, 0.7 mmol, 92%).

***N,N'*-Bis(1-isoquinolylmethyl)ethylenediamine (6b).** To the MeOH solution (30 mL) of isoquinoline-1-carboxaldehyde (600 mg, 3.82 mmol) was added ethylenediamine (0.13 mL, 1.91 mmol) in MeOH solution (10 mL) at 0 °C, and stirred for 1.5 h at r.t. After evaporation of the solvent, the residue was dissolved in EtOH (30 mL) and $NaBH_4$ (290 mg, 7.60 mmol) was added, then stirred overnight at r.t. After evaporation of the solvent, water was added and the product was extracted with $CHCl_3$. The organic layer was dried and evaporated to give compound **6b** as a brown oil (quant.). ^{1}H NMR ($CDCl_3$): δ 8.43 (d, J = 5.8 Hz, 2 H), 8.18 (d, J = 8.4 Hz, 2 H), 7.80 (d, J = 7.9 Hz, 2 H), 7.65 (ddd, J = 7.9, 7.0, 1.2 Hz, 2 H), 7.58 (ddd, J = 8.4, 7.0, 1.2 Hz, 2 H), 7.53 (d, J = 5.8 Hz, 2 H), 4.45 (s, 4 H), 3.01 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 158.6, 141.5, 136.0, 129.8, 127.2, 127.1, 126.6, 124.7, 124.5, 119.9, 52.5, 49.8. Anal Calcd. for $C_{22}H_{22}N_4$ (**6b**): H, 6.48; C, 77.16; N, 16.36. Found: H, 6.17; C, 77.26; N, 16.17.

***N,N'*-Bis(2-quinolylmethyl)-*N,N'*-bis(*tert*-butoxycarbonylmethyl)ethylenediamine (7a).** To the DMF solution (3 mL) of compound **6a** (1.03 g, 3.00 mmol) and *tert*-butyl bromoacetate (0.88 mL, 6.00 mmol) was added potassium carbonate (3.0 g, 20 mmol) and potassium iodide (2.0 g, 12 mmol), then stirred for 4 days at r.t. under N_2. After addition of water, the reaction mixture was extracted with $CHCl_3$ and the organic layer was washed with brine, dried, evaporated and washed with CH_3CN to give compound **7a** as a cream powder (1.56g, 2.73 mmol, 91%). ^{1}H NMR ($CDCl_3$): δ 8.57 (d, J = 8.5 Hz, 2 H), 8.36 (d, J = 5.8 Hz, 2 H), 7.74 (d, J = 8.1 Hz, 2 H), 7.59 (dd, J = 8.1, 7.0 Hz, 2 H), 7.51 (d, J = 5.8 Hz, 2 H), 7.43 (dd, J = 8.1, 7.2 Hz, 2 H), 4.29 (s, 4 H), 3.27 (s, 4 H), 2.80 (s, 4 H), 1.41 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 170.5, 158.2, 141.3, 136.2, 129.8, 127.7, 126.9, 126.7, 126.6, 120.5, 80.9, 59.7,

56.4, 52.0, 28.5. Anal Calcd. for $C_{34}H_{42}N_4O_4$ (**7a**): H, 7.42; C, 71.55; N, 9.82. Found: H, 7.22; C, 71.27; N, 9.42.

***N,N'*-Bis(1-isoquinolylmethyl)-*N,N'*-bis(*tert*-butoxycarbonylmethyl)ethylenediamine (7b).** To the DMF solution (3 mL) of compound **6b** (500 mg, 1.46 mmol) and *tert*-butyl bromoacetate (0.43 mL, 2.92 mmol) was added potassium carbonate (1.60 g, 11.6 mmol) and potassium iodide (970 mg, 5.84 mmol), then stirred for 4.5 days at r.t. under N_2. After addition of water, the reaction mixture was extracted with ethyl acetate and the organic layer was washed with brine, dried and evaporated to give compound **7b** as an orange oil (713 mg, 1.25 mmol, 86%). ^{1}H NMR ($CDCl_3$): δ 8.57 (d, *J* = 8.2 Hz, 2 H), 8.35 (d, *J* = 5.8 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 7.59 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2 H), 7.51 (d, *J* = 5.5 Hz, 2 H), 7.43 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2 H), 4.29 (s, 4 H), 3.27 (s, 4 H), 2.80 (s, 4 H), 1.41 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 170.5, 158.2, 141.3, 129.8, 127.7, 126.9, 126.7, 126.6, 120.4, 100.1, 80.8, 59.7, 56.4, 52.0, 28.5. Anal Calcd. for $C_{34}H_{42}N_4O_4$ (**7b**·$0.3H_2O$): H, 7.45; C, 70.88; N, 9.72. Found: H, 7.44; C, 70.85; N, 9.65.

***N,N*-Bis(2-quinolylmethyl)-*N',N'*-bis(ethoxycarbonylmethyl)ethylenediamine (*N,N*-BQENDA-Et).** To the CH_3CN solution (15 mL) of compound **4b** (390 mg, 1.14 mmol) and ethyl bromoacetate (0.25 mL, 2.28 mmol) was added potassium carbonate (1.3 g, 9.4 mmol) and potassium iodide (740 mg, 7.83 mmol), then stirred at 60 °C under N_2 for 2 days. The resultant solution was cooled to r.t. and the solvent was evaporated. After addition of $CHCl_3$, the precipitate was filtered and the filtrate was evaporated and purified by column chromatography (alumina, AcOEt/hexane 10/1, R_f = 0.4) to give *N,N*-BQENDA-Et as an orange oil (264 mg, 0.5 mmol, 45%). ^{1}H NMR ($CDCl_3$): δ 8.12 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.70-7.79 (m, 4H), 7.67 (ddd, *J* = 8.2, 7.0, 1.5 Hz, 2H), 7.49 (dd, *J* = 7.9, 0.9 Hz, 2H), 4.01-4.08 (m, 8H), 3.51 (s, 4H), 3.00 (dd, *J* = 6.4, 7.3 Hz, 2H), 2.80 (dd, *J* = 7.6, 6.1 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 171.0, 160.2, 147.4, 136.2, 129.3,

129.0, 127.4, 127.3, 126.1, 121.2, 61.7, 60.6, 55.2, 52.7, 52.1, 14.5. Anal Calcd. for $C_{30}H_{34}N_4O_4$ (*N,N*-BQENDA-Et): H, 6.66; C, 70.02; N, 10.89. Found: H, 6.70; C, 70.22; N, 10.80.

***N,N*-Bis(1-isoquinolylmethyl)-*N',N'*-bis(ethoxycarbonylmethyl)ethylenediamine (*N,N*-1-isoBQENDA-Et).** To the CH_3CN solution (10 mL) of compound **4b** (70 mg, 0.2 mmol) and ethyl bromoacetate (0.05 mL, 0.4 mmol) was added potassium carbonate (220 mg, 1.6 mmol) and potassium iodide (130 mg, 0.8 mmol), then stirred at 60 °C under N_2 for 2 days. The resultant solution was cooled to r.t. and the solvent was evaporated. After addition of $CHCl_3$, the precipitate was filtered and the filtrate was evaporated and purified by column chromatography (alumina, AcOEt/hexane 10/1, R_f = 0.4) to give *N,N*-1-isoBQENDA-Et as a yellow oil (62 mg, 0.12 mmol, 60%). ^{1}H NMR ($CDCl_3$): δ 8.43 (d, *J* = 5.8 Hz, 2H), 8.16 (d, *J* = 7.9 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.54-7.61 (m, 4H), 7.23 (dd, *J* = 8.9, 8.2 Hz, 2H), 4.23 (s, 4H), 4.00 (q, *J* = 7.2 Hz, 4H), 3.35 (s, 4H), 2.97 (dd, *J* = 6.4, 6.4 Hz, 2H), 2.73 (dd, *J* = 6.1, 6.7 Hz, 2H), 1.14 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 170.8, 158.4, 141.4, 136.2, 129.8, 127.6, 127.2, 126.6, 126.6, 120.6, 60.4, 60.3, 54.4, 52.4, 50.7, 14.5. Anal Calcd. for $C_{30}H_{34}N_4O_4$ (*N,N*-1-isoBQENDA-Et): H, 6.66; C, 70.02; N, 10.89. Found: H, 6.68; C, 69.80; N, 10.68.

References

(1) Ichimura, C.; Shiraishiaaa, Y.; Hirai, T. *Tetrahedron* **2010**, *66*, 5594-5601.

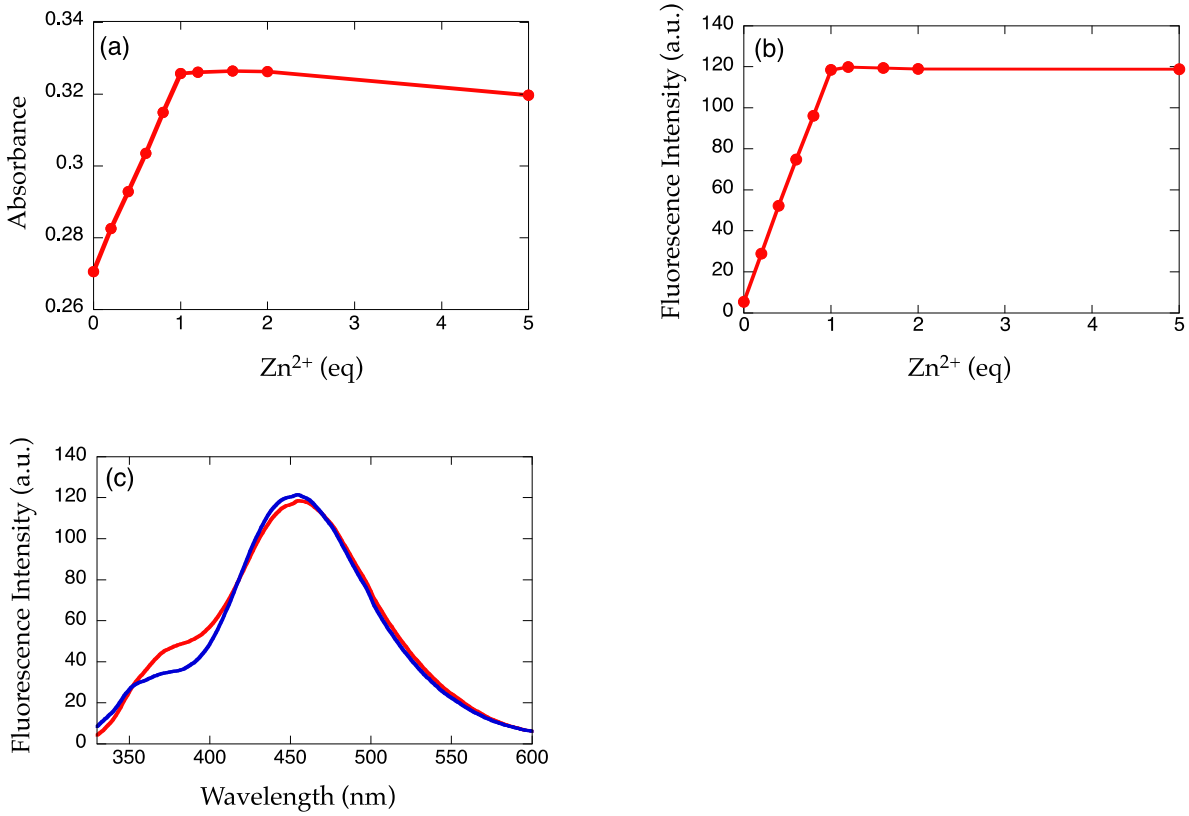


Fig. S1. Zinc titration profile for 34 μM **1a** in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 25 °C. (a) UV-vis absorbance changes at 303 nm. (b) Fluorescence intensity changes (λ_{ex} = 315 nm) at 456 nm. (c) Overlay of the fluorescence spectra for 34 μM [Zn(**1a**)] in HEPES buffer (red) and DMF/water (1:1) (blue).

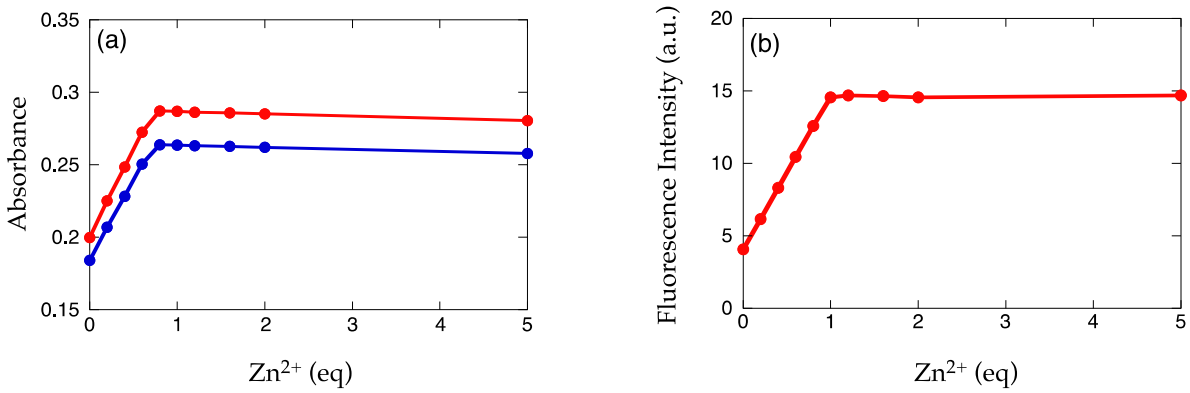


Fig. S2. Zinc titration profile for 34 μM **2a** in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 25 °C. (a) UV-vis absorbance changes at 304 (red) and 317 nm (blue). (b) Fluorescence intensity changes at 377 nm (λ_{ex} = 317 nm).

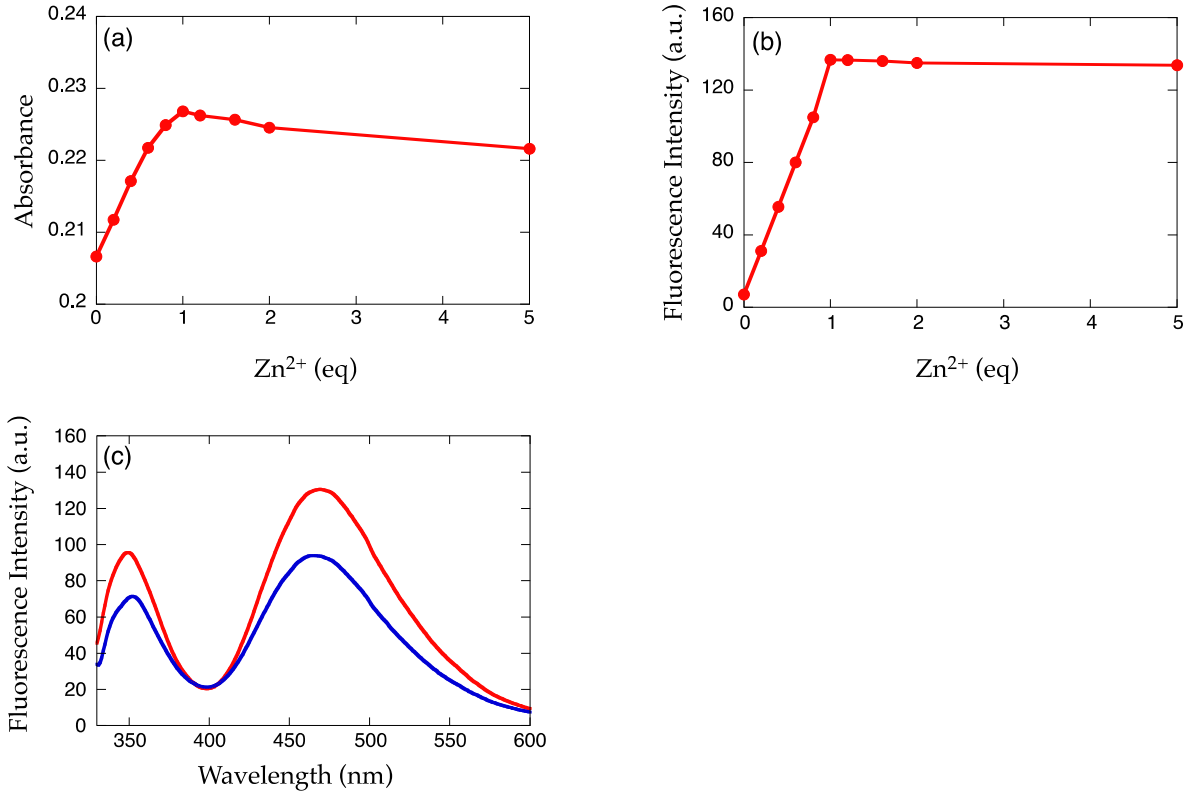
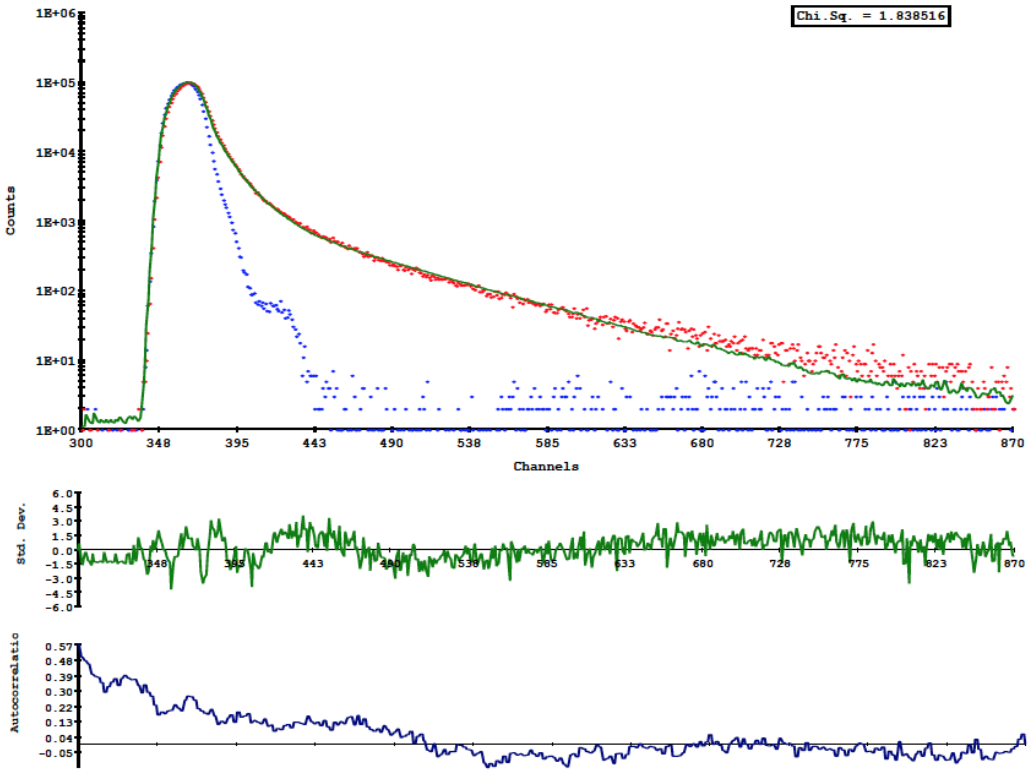


Fig. S3. Zinc titration profile for 34 μM **1b** in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 25 °C. (a) UV-vis absorbance changes at 311 nm. (b) Fluorescence intensity changes (λ_{ex} = 324 nm) at 469 nm. (c) Overlay of the fluorescence spectra for 34 μM **[**Zn**(1b)]** in HEPES buffer (red) and DMF/water (1:1) (blue).

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Calculated using 3 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 30       ch;         1.677618E-09   sec

 T1 Estimate = 3.476334 ch;         1.943987E-10   sec
 T2 Estimate = 6.952667 ch;         3.887973E-10   sec
 T3 Estimate = 13.90533 ch;         7.775947E-10   sec

 A Free
 B1 Free
 B2 Free
 B3 Free

 Prompt and decay LO = 300    ch;   1.677618E-08   sec
 Prompt and decay HI = 900    ch;   5.032854E-08   sec

 Background on prompt = 0.4285714
 Time calibration = 5.59206E-11 sec/ch

The fitted parameters are:

 Hi reduced to: 870 ch

 SHIFT = -7.224151E-02 ch;   -4.039789E-12 sec     S.Dev = 5.208623E-13  sec
 T1    = 1.823967      ch;   1.019973E-10  sec     S.Dev = 2.748593E-12  sec
 T2    = 12.41462      ch;   6.942332E-10  sec     S.Dev = 6.234594E-12  sec
 T3    = 63.74554      ch;   3.564689E-09  sec     S.Dev = 2.93196E-11   sec
 A     = 1.083236                                 S.Dev = 0.1209284
 B1    = 0.6006663     [ 75.59 Rel.Ampl][ 0.96 Alpha] S.Dev = 6.932129E-04
 B2    = 2.387014E-02  [ 20.45 Rel.Ampl][ 0.04 Alpha] S.Dev = 7.494076E-05
 B3    = 9.016765E-04  [ 3.97 Rel.Ampl][ 0.00 Alpha] S.Dev = 4.367985E-06
 Average Life Time = 1.295923E-10  sec
 CHISQ = 1.838516            [ 563 degrees of freedom ]

Chi-squared Probability = 1.9288E-20 percent
Durbin-Watson Parameter =  0.8641922
Negative residuals      =   41.50613 percent
Residuals < 1 s.dev     =   47.11033 percent
Residuals < 2 s.dev     =   87.91594 percent
Residuals < 3 s.dev     =   98.07355 percent
Residuals < 4 s.dev     =   99.82487 percent
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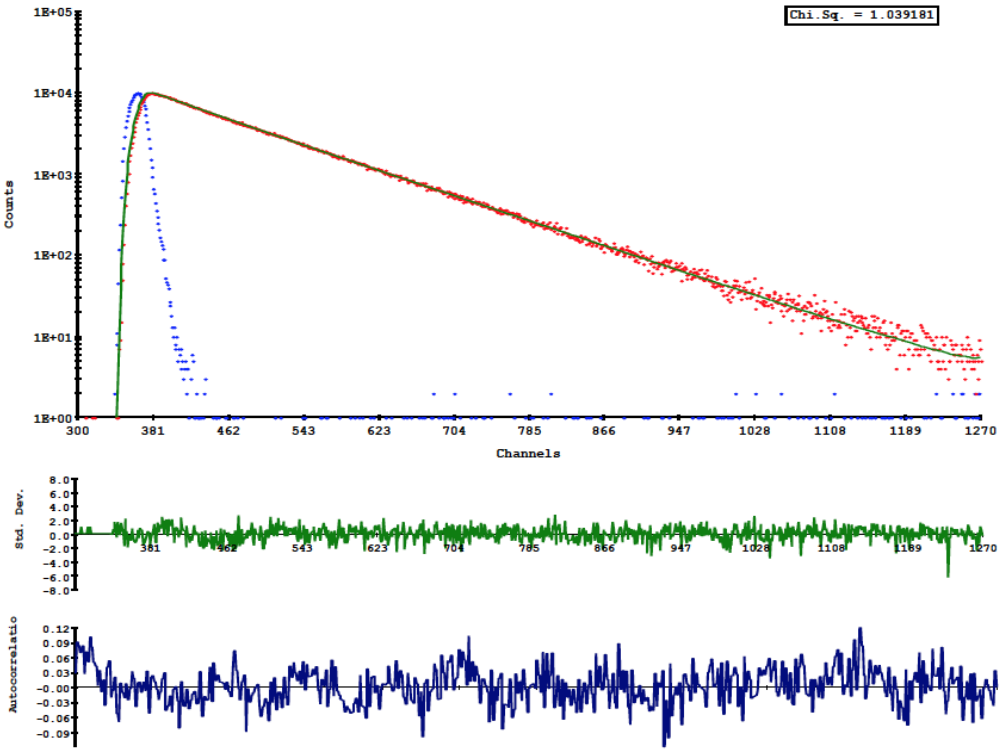
Fig. S4. Fluorescence lifetime measurement for 34 μM **1b** in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 351 nm (λ_{ex} = 333 nm, 25 °C).

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Calculated using 2 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0        ch;         0               sec
 Shift Limit = 30       ch;         1.677618E-09    sec

 T1 Estimate = 55.15411 ch;         3.084251E-09    sec
 T2 Estimate = 220.6165 ch;         1.233701E-08    sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 300    ch;   1.677618E-08    sec
 Prompt and decay HI = 1300   ch;   7.269678E-08    sec

 Background on prompt = 5.128205E-02
 Time calibration = 5.59206E-11 sec/ch

The fitted parameters are:

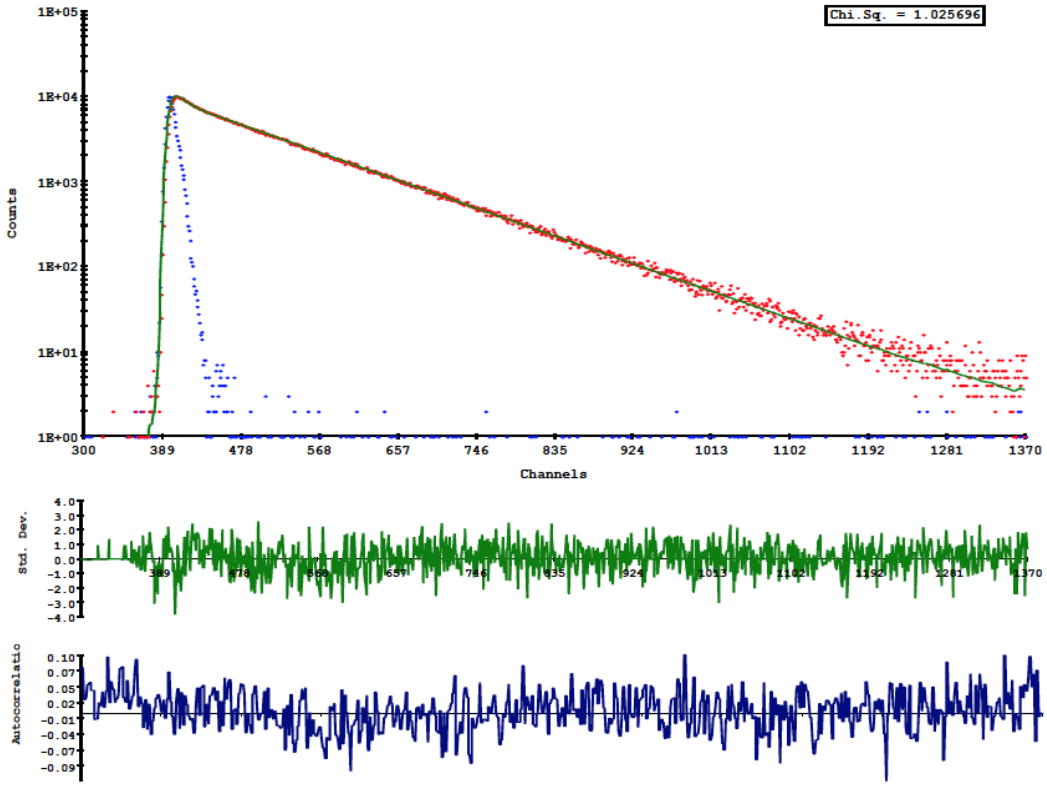
 Hi reduced to: 1270 ch

 SHIFT = 1.526547      ch;   8.536541E-11  sec     S.Dev = 1.634499E-12  sec
 T1    = 56.59895      ch;   3.165047E-09  sec     S.Dev = 5.20767E-11   sec
 T2    = 113.9156      ch;   6.370227E-09  sec     S.Dev = 1.363356E-11  sec
 A     = -8.410214E-02                           S.Dev = 0.1199274
 B1    = 6.105802E-03  [ 5.60 Rel.Ampl][ 0.11 Alpha] S.Dev = 1.688319E-04
 B2    = 5.113079E-02  [ 94.40 Rel.Ampl][ 0.89 Alpha] S.Dev = 9.554063E-05
 Average Life Time = 6.028309E-09  sec
 CHISQ = 1.039181            [ 965 degrees of freedom ]

 Chi-squared Probability =   19.37004 percent
 Durbin-Watson Parameter =   1.941699
 Negative residuals      =   43.97528 percent
 Residuals < 1 s.dev     =     69.207 percent

Residuals < 2 s.dev     =   94.54171 percent
Residuals < 3 s.dev     =   99.58805 percent
Residuals < 4 s.dev     =   99.89701 percent
```

Fig. S5. Fluorescence lifetime measurement for 34 μM **1b** in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 469 nm (λ_{ex} = 333 nm, 25 °C).




```
Calculated using 2 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 30       ch;         1.677618E-09   sec

 T1 Estimate = 55.20351 ch;         3.087013E-09   sec
 T2 Estimate = 220.814  ch;         1.234805E-08   sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 300    ch;   1.677618E-08   sec
 Prompt and decay HI = 1400   ch;   7.828884E-08   sec

 Background on prompt = 0.5487805
 Time calibration = 5.59206E-11 sec/ch

The fitted parameters are:

 Hi reduced to: 1370 ch

 SHIFT = 0.3033262     ch;   1.696219E-11  sec     S.Dev = 1.446836E-12  sec
 T1    = 7.430247      ch;   4.155039E-10  sec     S.Dev = 1.385584E-11  sec
 T2    = 118.3029      ch;   6.61557E-09   sec     S.Dev = 7.546992E-12  sec
 A     = -0.0408564                               S.Dev = 9.219646E-02
 B1    = 7.174253E-02  [ 5.81 Rel.Ampl][ 0.50 Alpha] S.Dev = 5.965266E-04
 B2    = 7.302698E-02  [ 94.19 Rel.Ampl][ 0.50 Alpha] S.Dev = 7.712415E-05
 Average Life Time = 3.543042E-09  sec
 CHISQ = 1.025696            [ 1065 degrees of freedom ]

 Chi-squared Probability =   27.35546 percent
 Durbin-Watson Parameter =   1.836285
 Negative residuals      =   47.24556 percent
 Residuals < 1 s.dev     =   67.88049 percent


Residuals < 2 s.dev     =   94.77124 percent
Residuals < 3 s.dev     =   99.62652 percent
Residuals < 4 s.dev     =         100 percent
```

Fig. S6. Fluorescence lifetime measurement for 34 μM **1a** in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 456 nm (λ_{ex} = 295 nm, 25 °C).

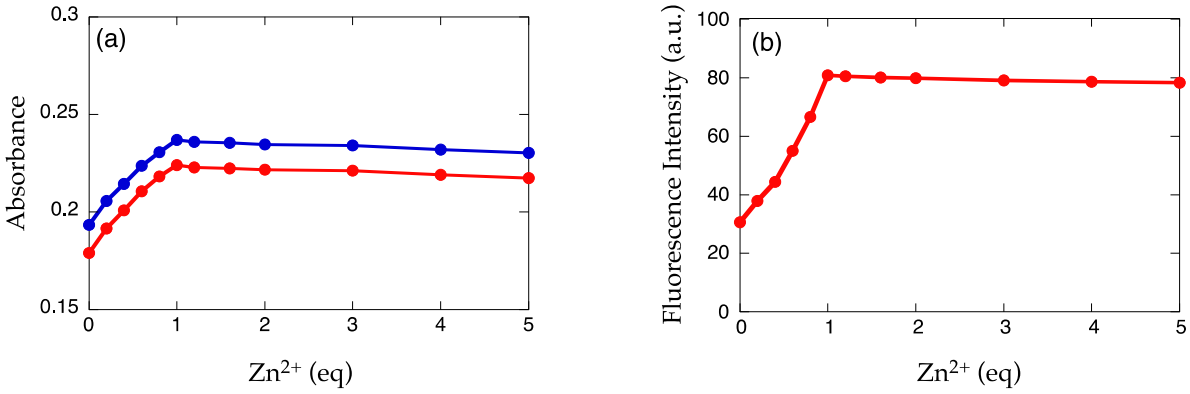


Fig. S7. Zinc titration profile for 34 μM **2b** in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 25 °C. (a) UV-vis absorbance changes at 313 (red) and 323 nm (blue). (b) Fluorescence intensity changes (λ_{ex} = 324 nm) at 352 nm.

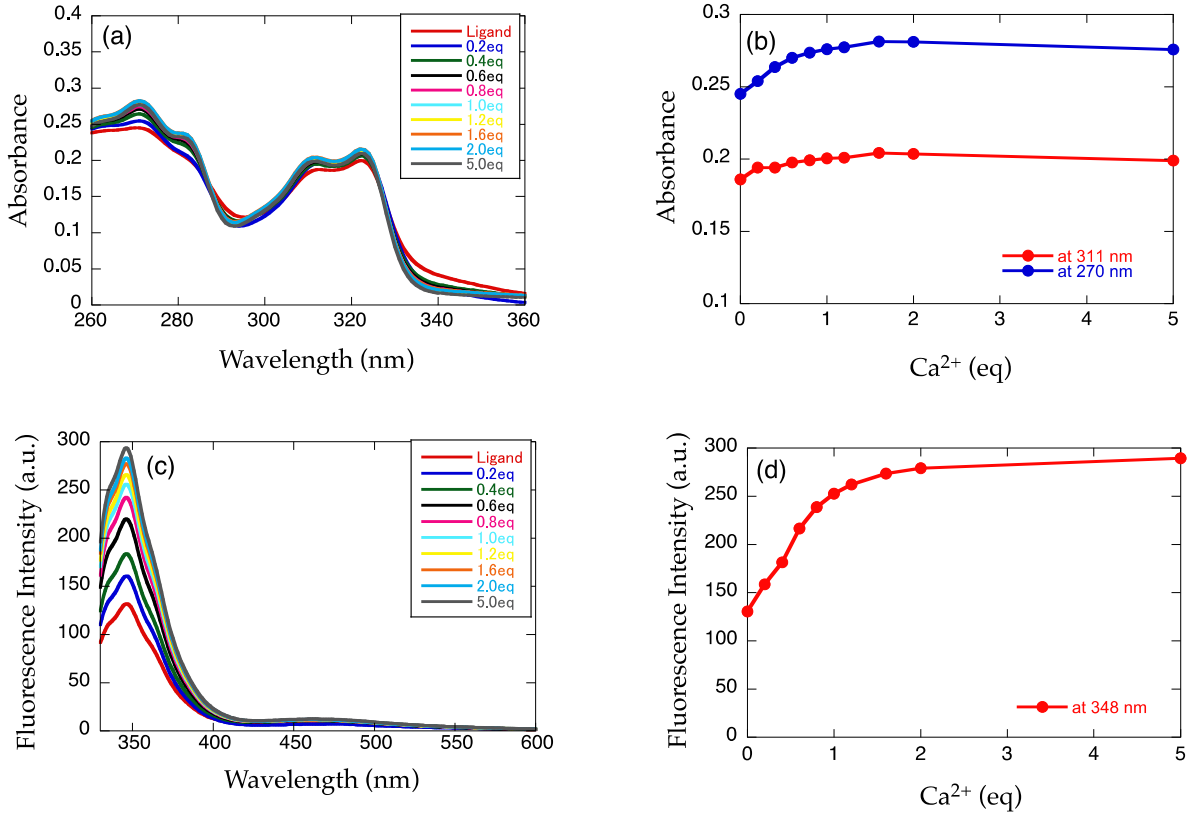


Fig. S8. Calcium titration profile for 34 μM **1b** in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 25 °C. (a) UV-vis absorbance spectral changes. (b) UV-vis absorbance changes at 270 and 311 nm. (c) Fluorescence spectral changes (λ_{ex} = 324 nm). (d) Fluorescence intensity changes at 348 nm.

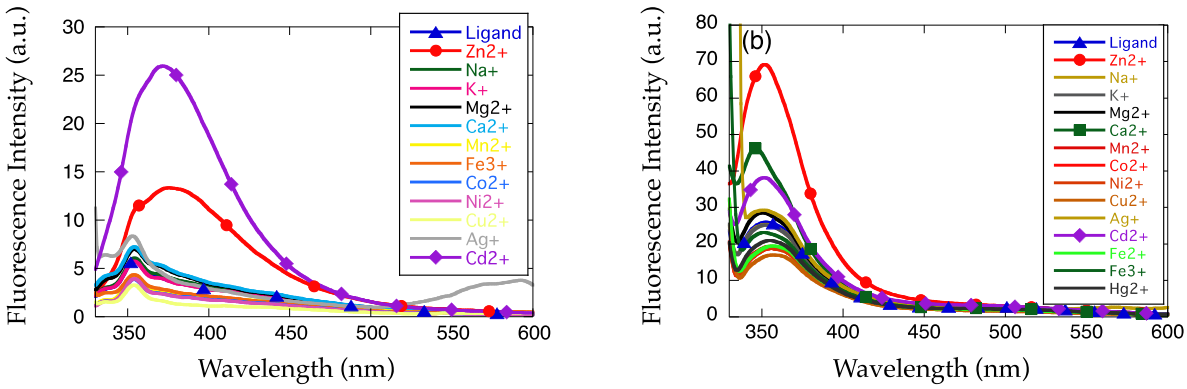


Fig. S9. Comparison of fluorescence spectra of 34 μM (a) **2a** (λ_{ex} = 317 nm) and (b) **2b** (λ_{ex} = 324 nm) in 50 mM HEPES buffer containing 0.10 M KCl (pH = 7.50) at 25 °C in the presence of 1 equivalent of zinc (red, circles), cadmium (blue, squares) and other metal ions (various colors, no marks).

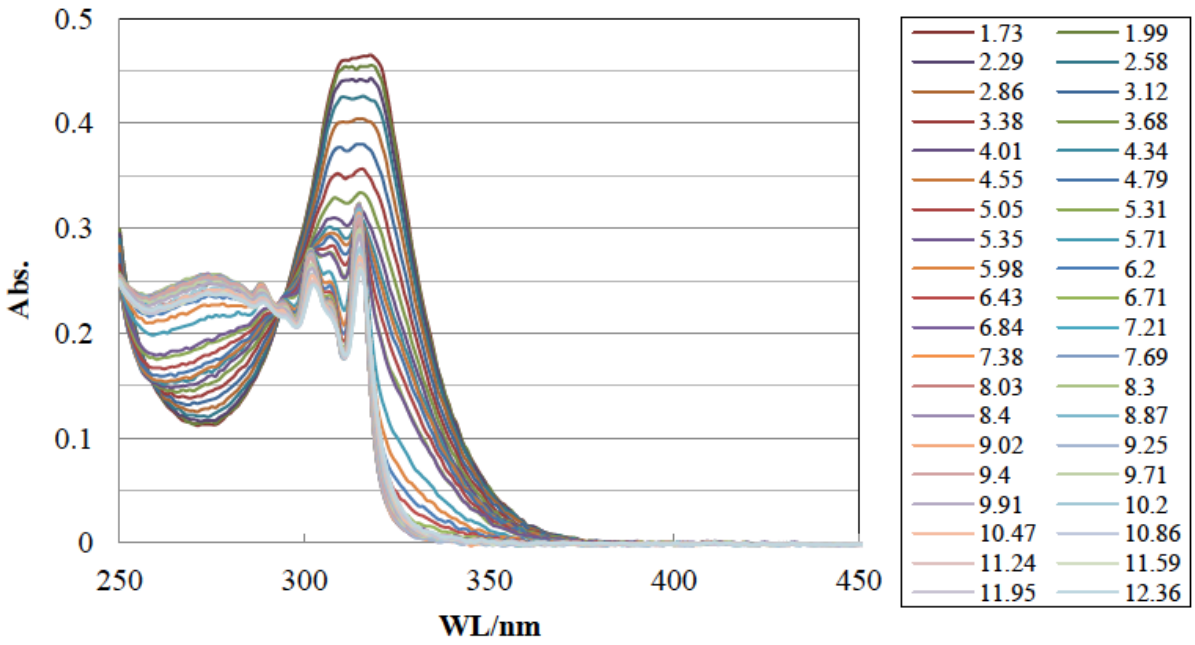


Fig. S10. UV-Vis spectra of **1a** at various pHs. C_L = 35.3 μM and pH = 1.73-12.36 with I = 0.1 M (KCl) at 25 °C.

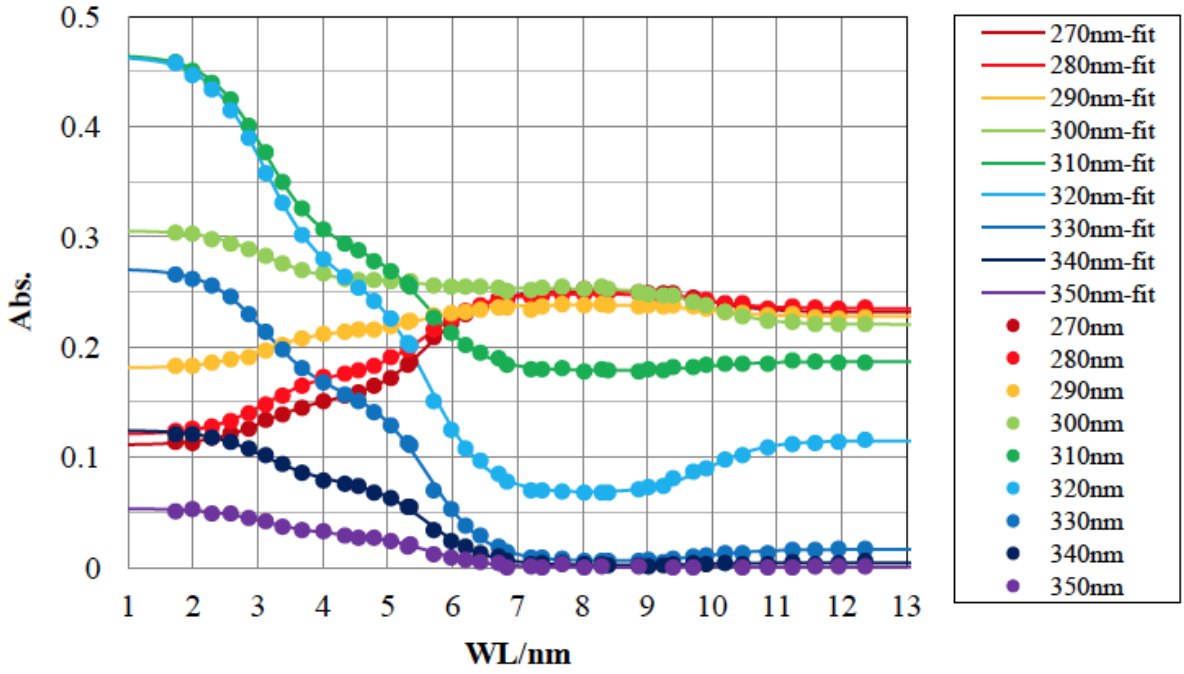


Fig. S11. Absorbance vs. pH plots in Fig. S7.

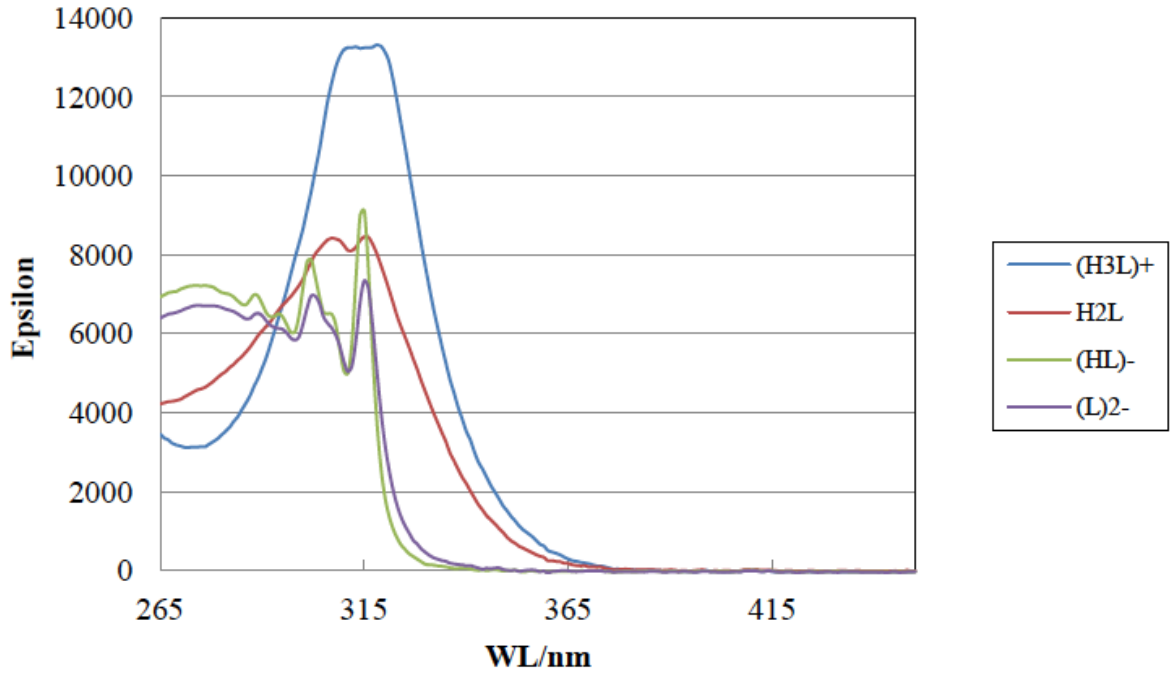


Fig. S12. UV-Vis spectra of the species involved in acid dissociation equilibrium of **1a**.

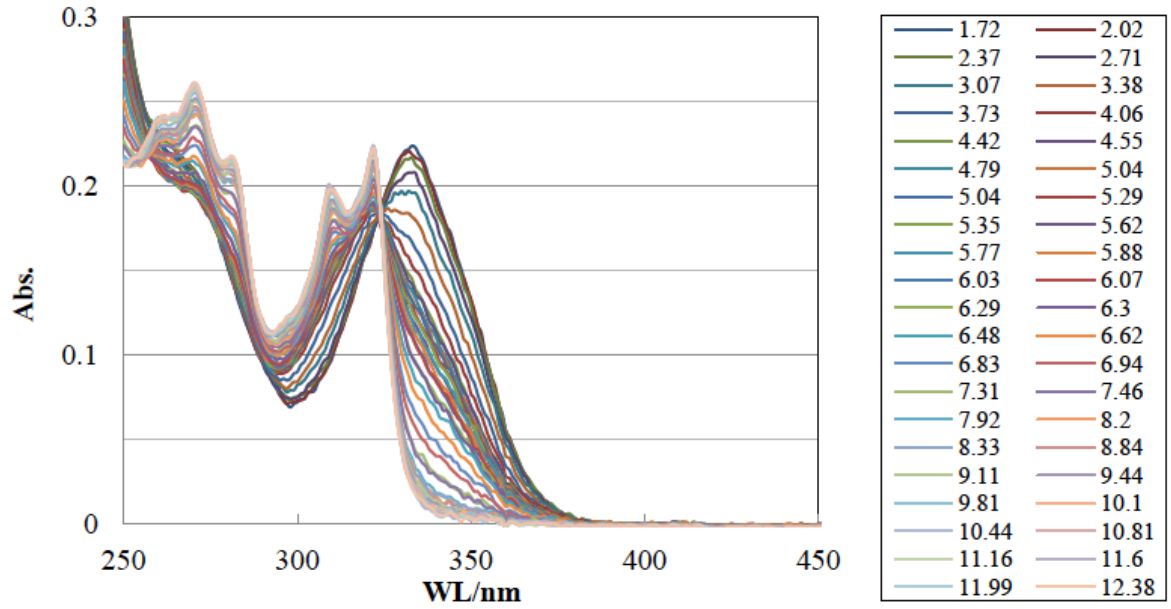


Fig. S13. UV-Vis spectra of **1b** at various pHs. C_L = 36.4 μM and pH = 1.72-12.38 with I = 0.1 M (KCl) at 25 °C.

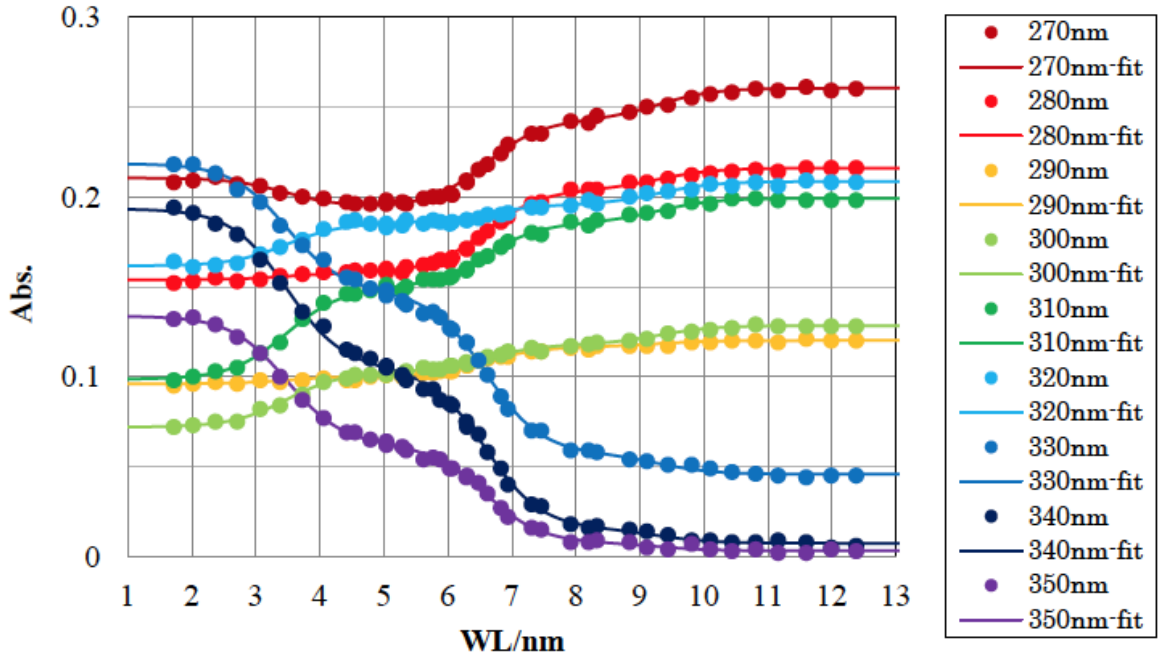


Fig. S14. Absorbance vs. pH plots in Fig. S10.

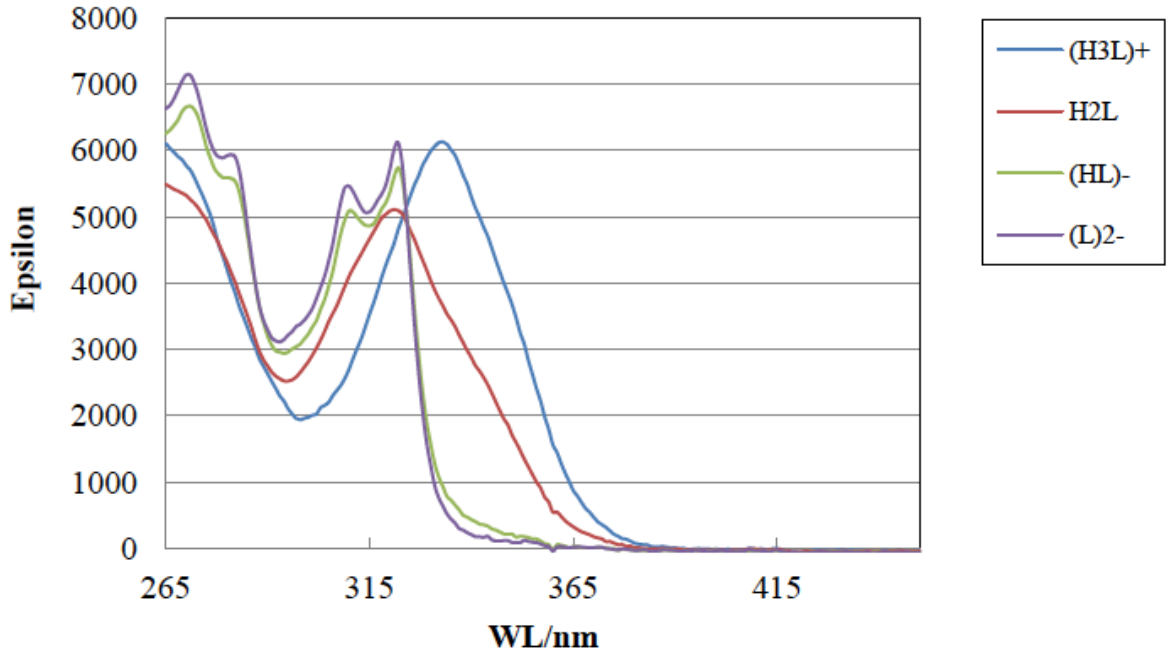


Fig. S15. UV-Vis spectra of the species involved in acid dissociation equilibrium of **1b**.

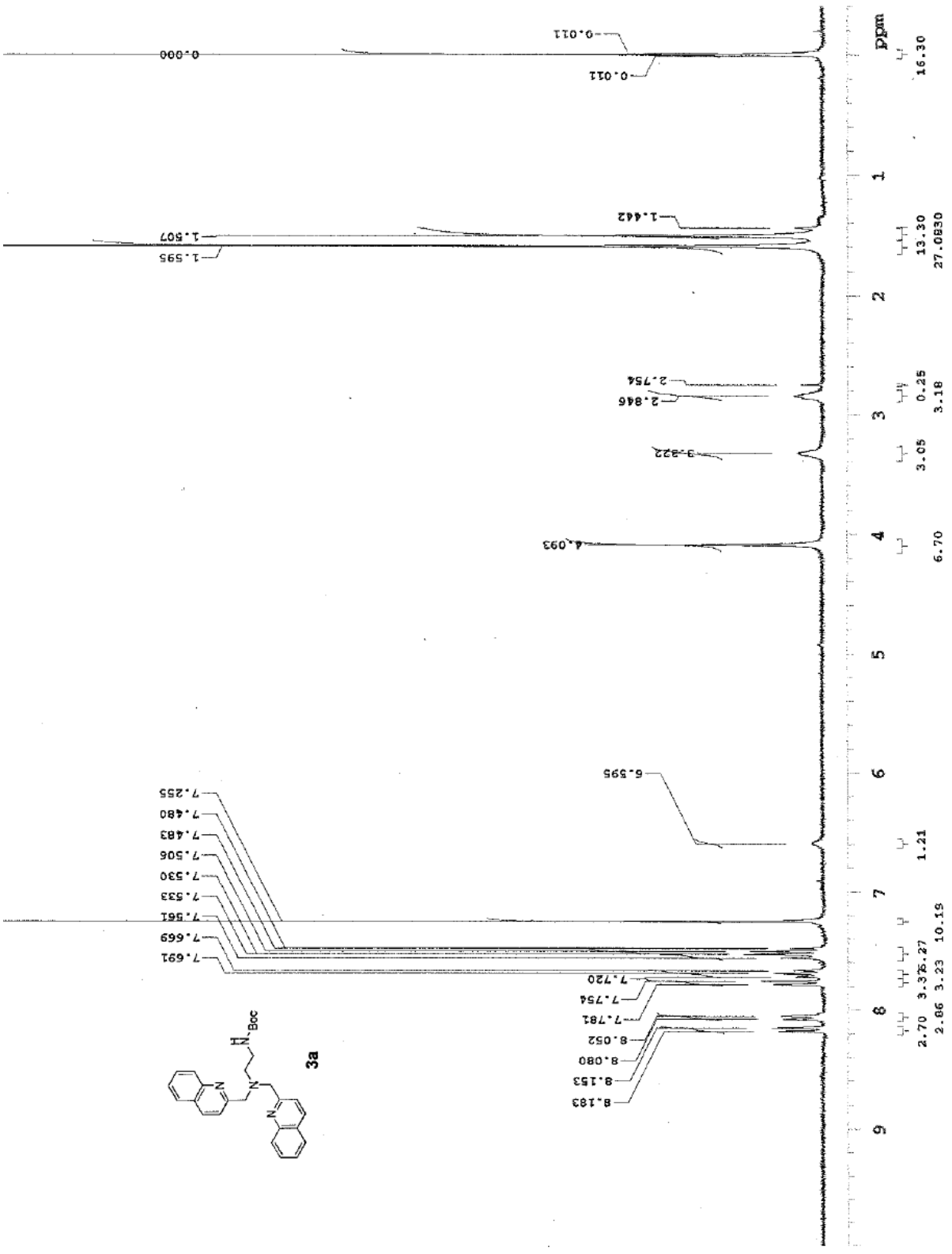


Fig. S16. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

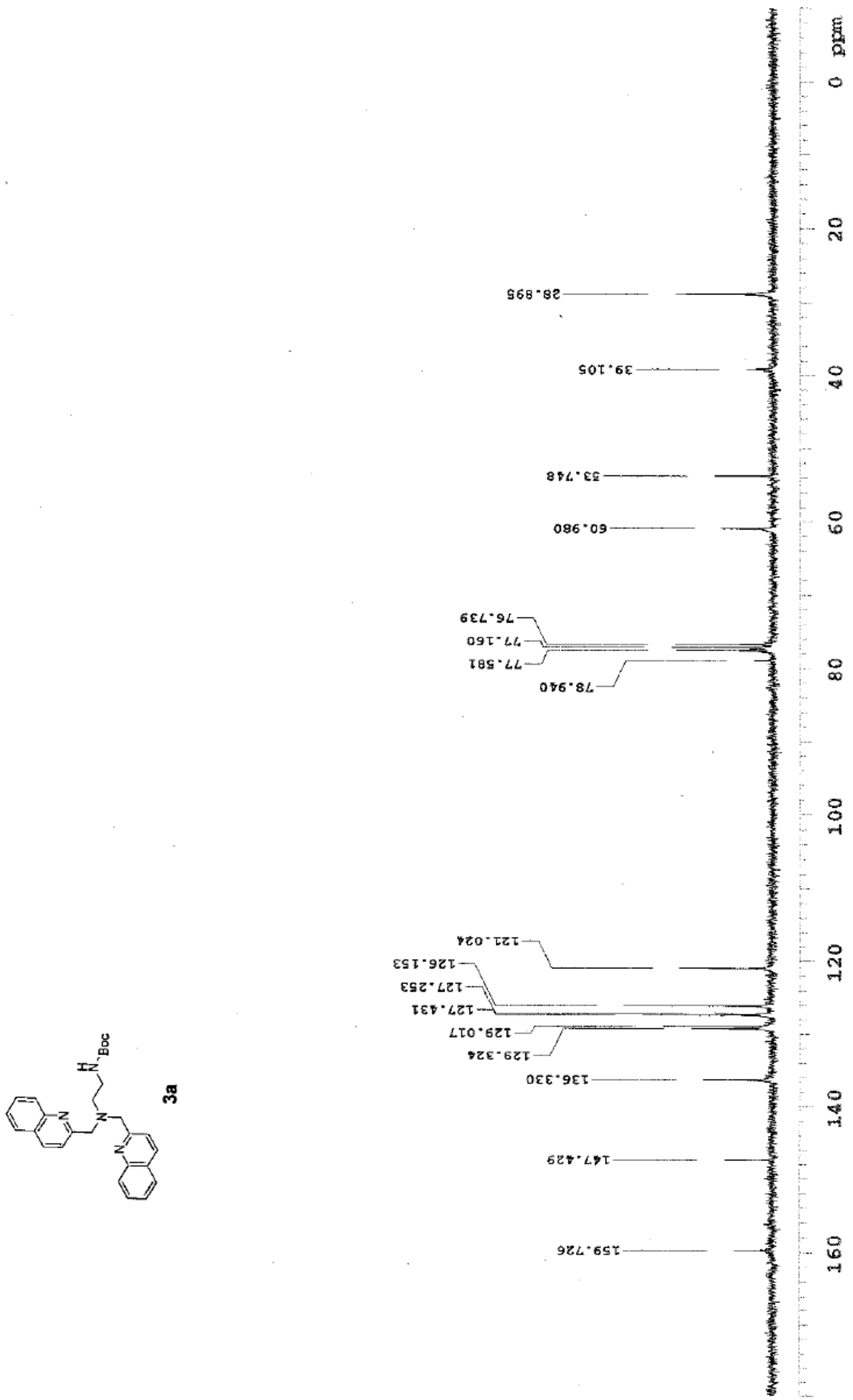


Fig. S17. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

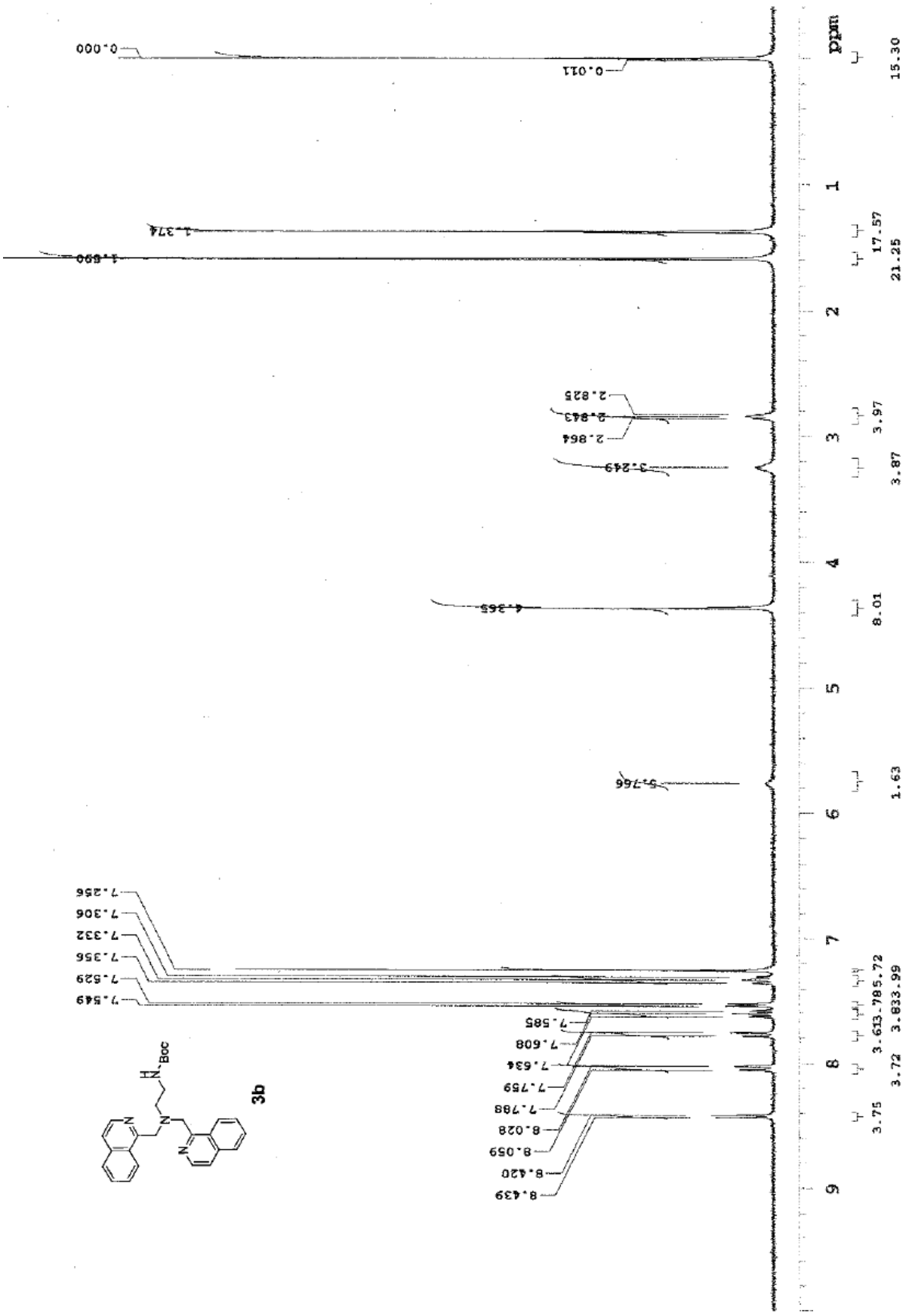


Fig. S18. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

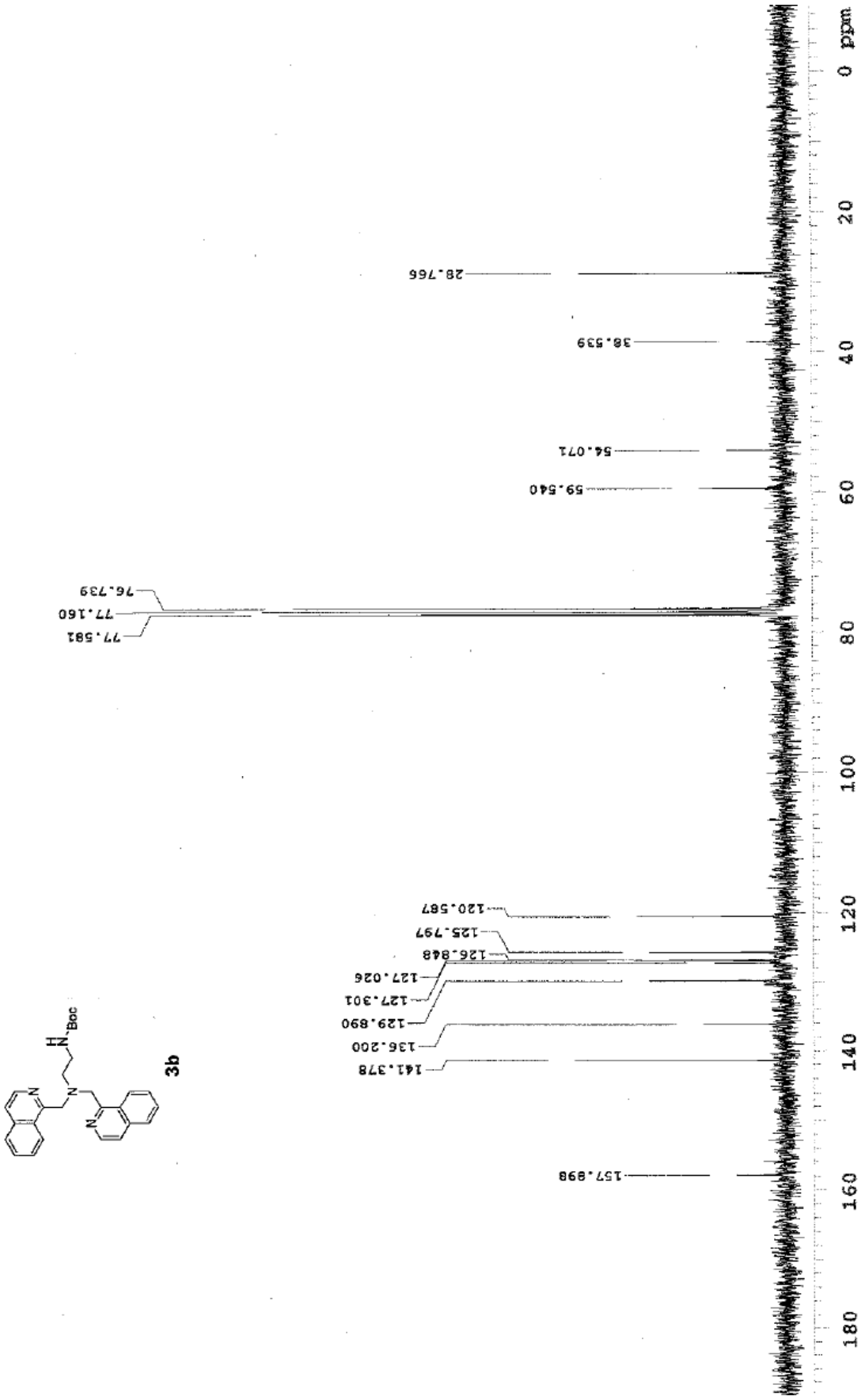


Fig. S19. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

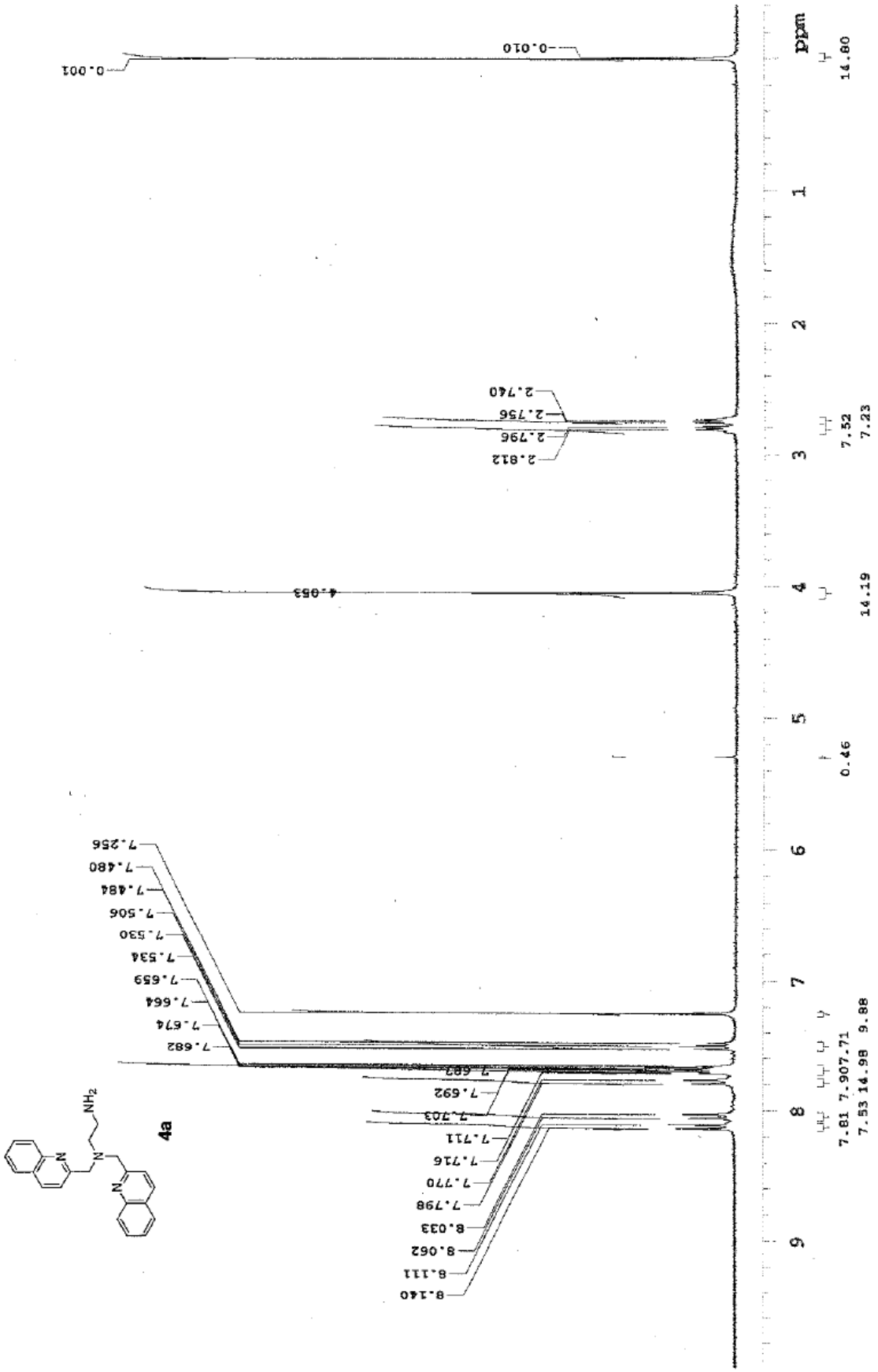


Fig. S20. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

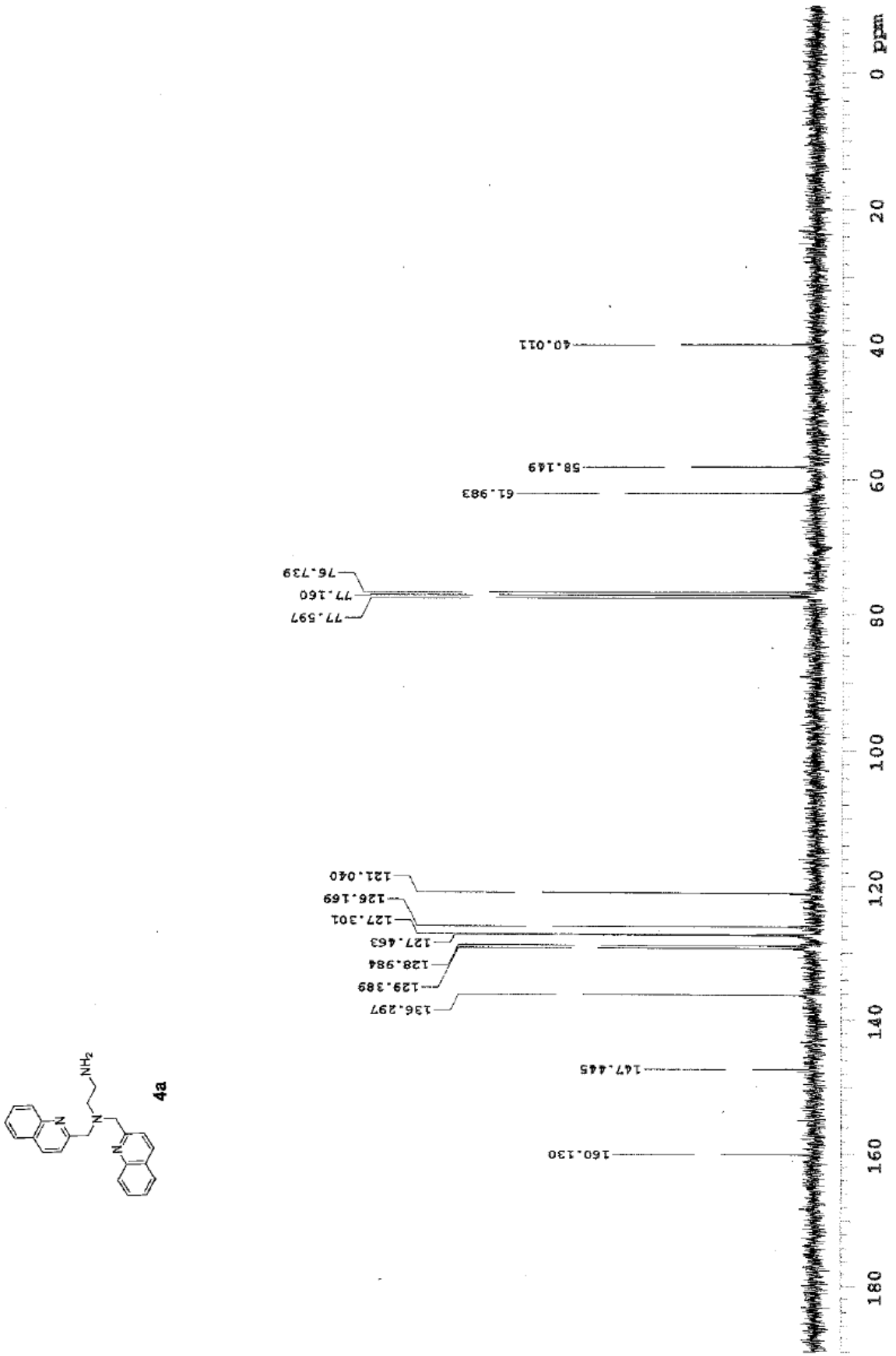


Fig. S21. ^{13}C NMR spectrum of **4a** in $CDCl_3$.

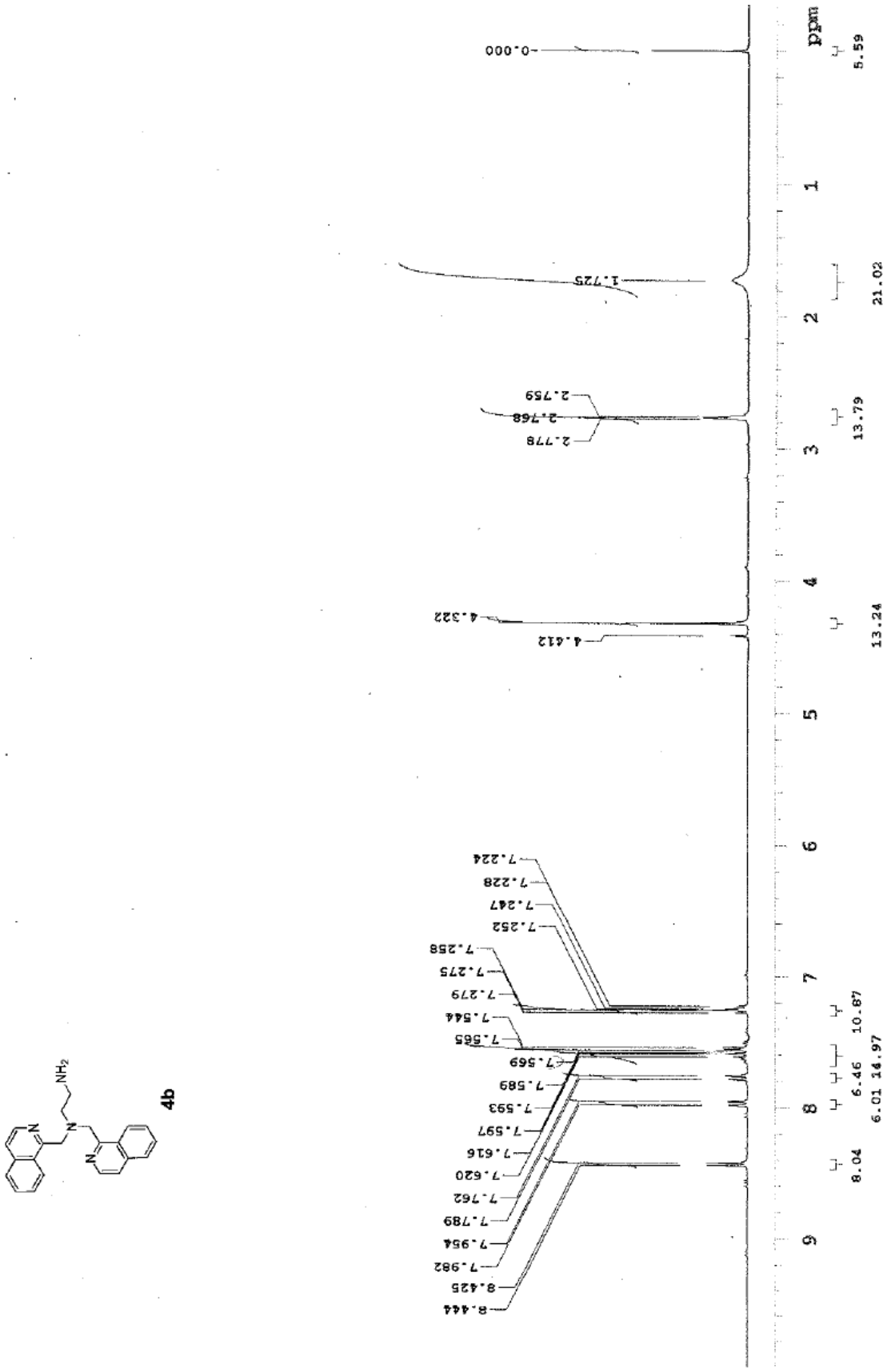


Fig. S22. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

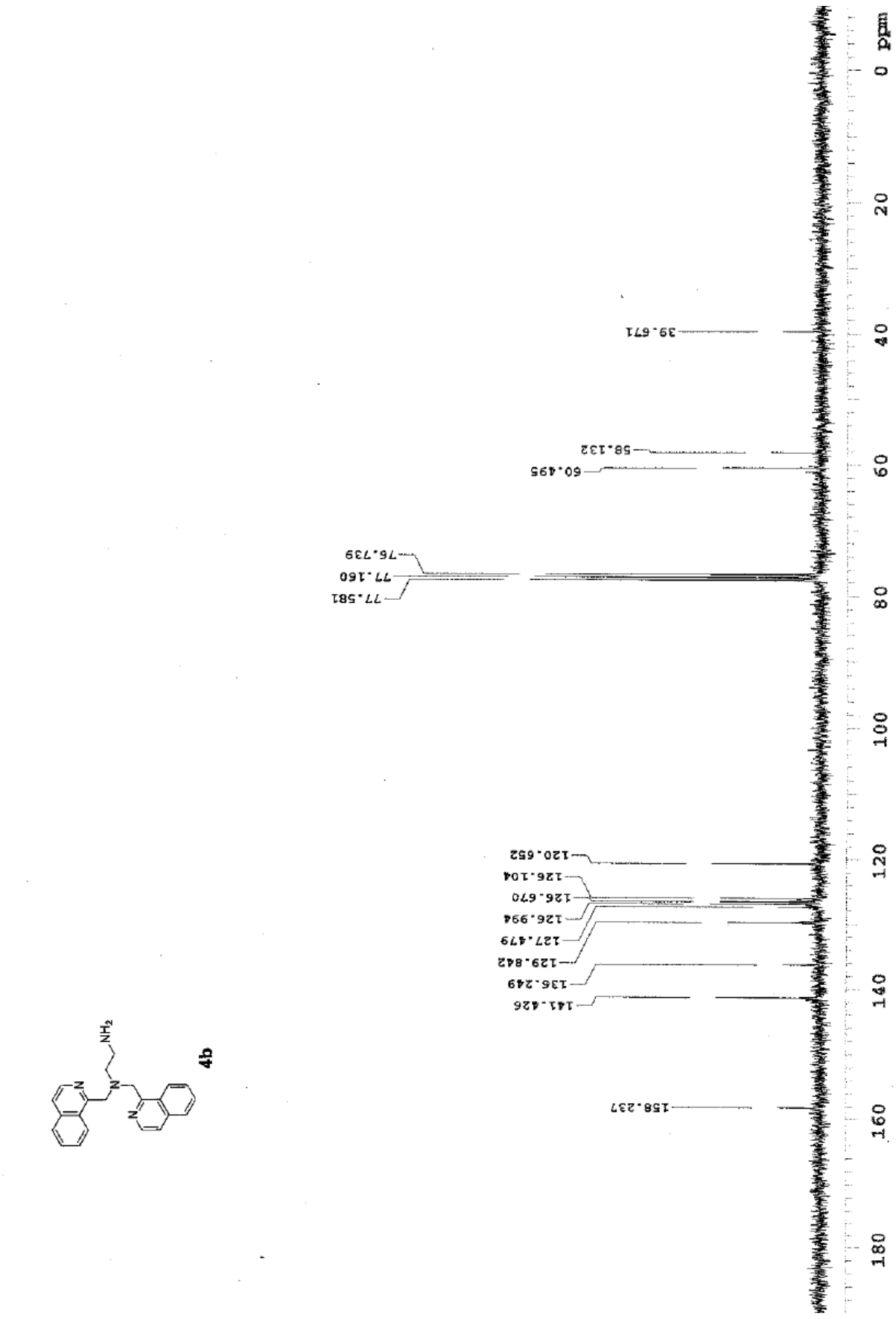


Fig. S23. ^{13}C NMR spectrum of **4b** in $CDCl_3$.

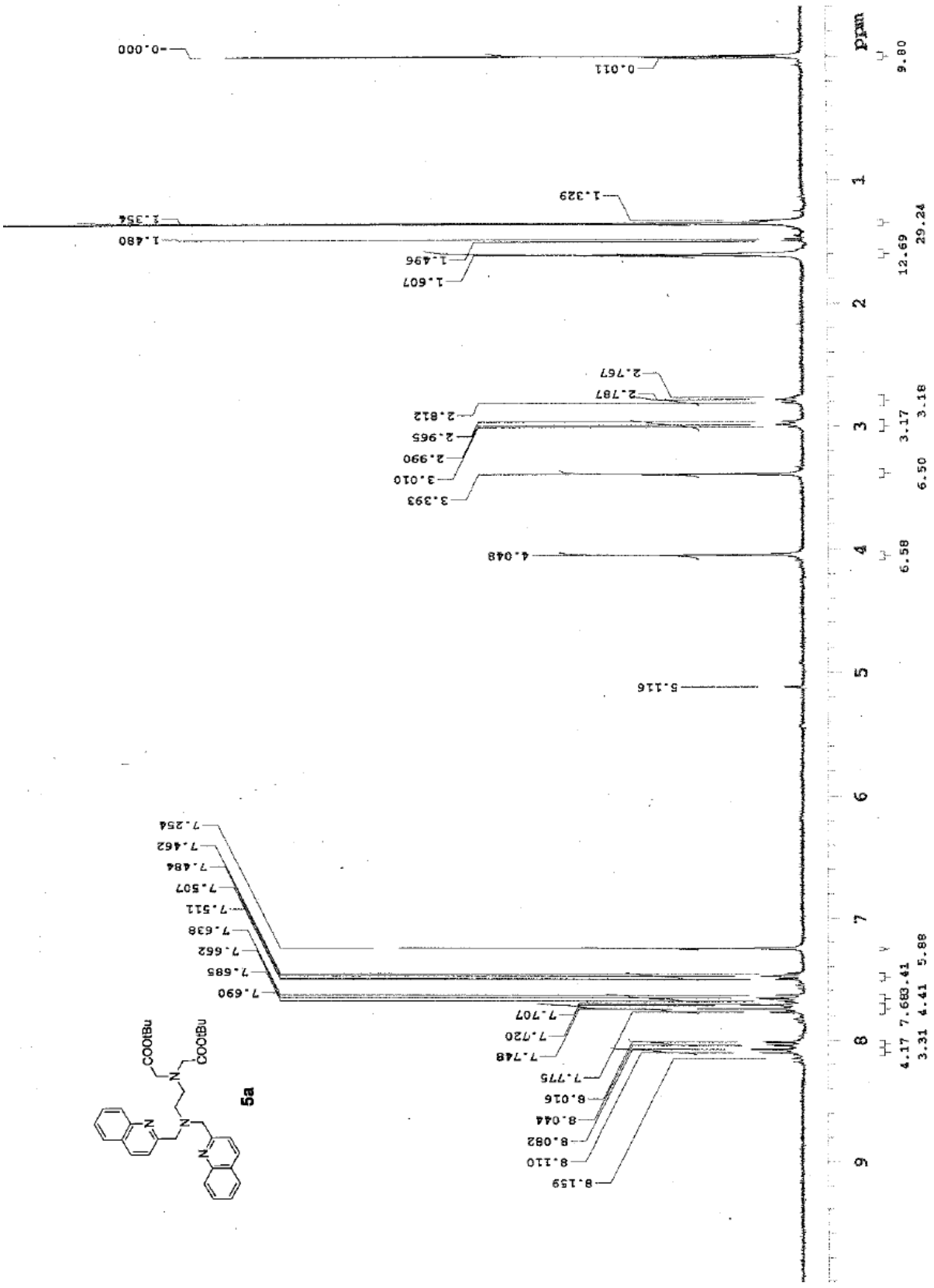


Fig. S24. ^{1}H NMR spectrum of **5a** in $CDCl_3$.

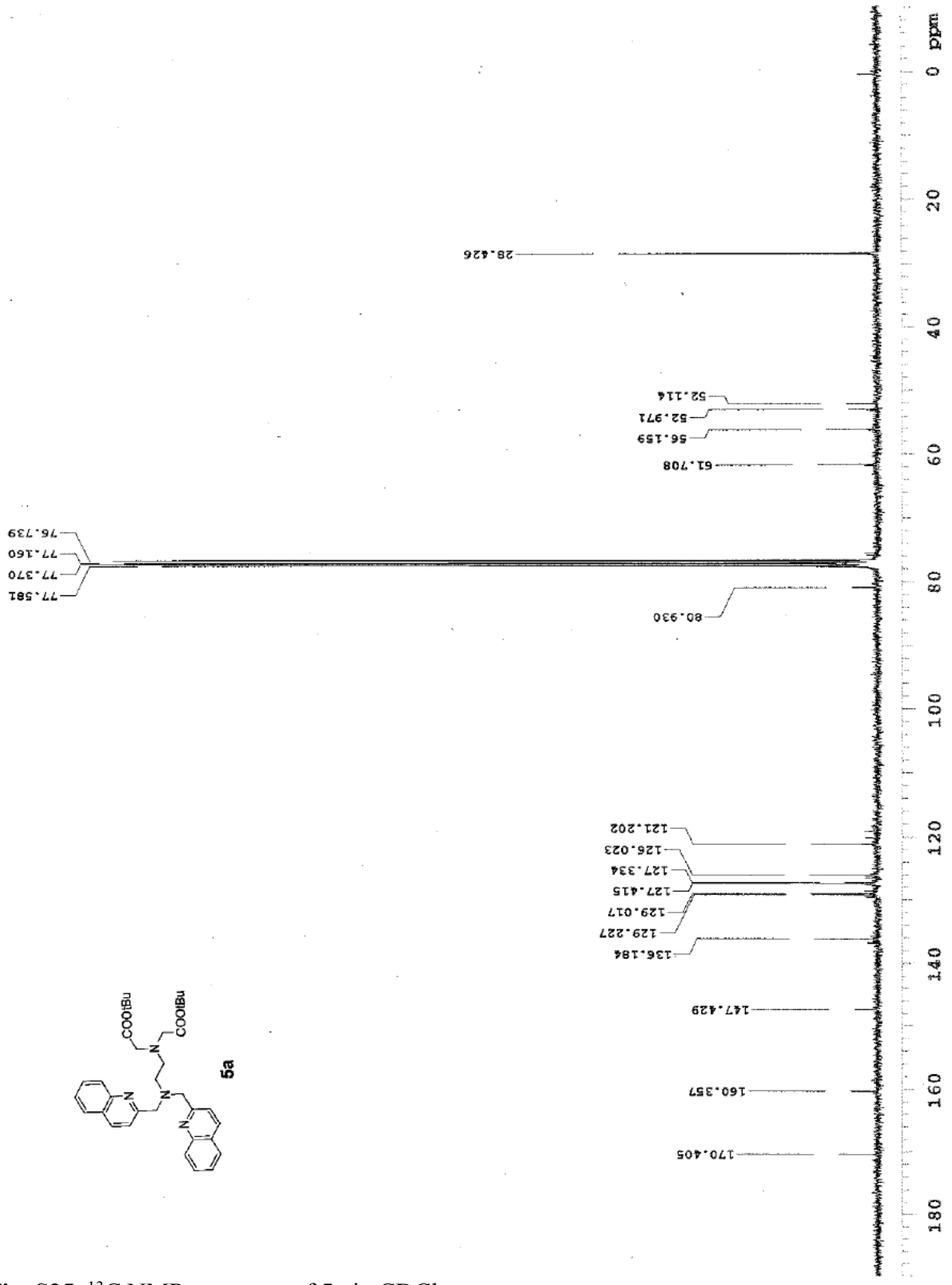


Fig. S25. ^{13}C NMR spectrum of **5a** in $CDCl_3$.

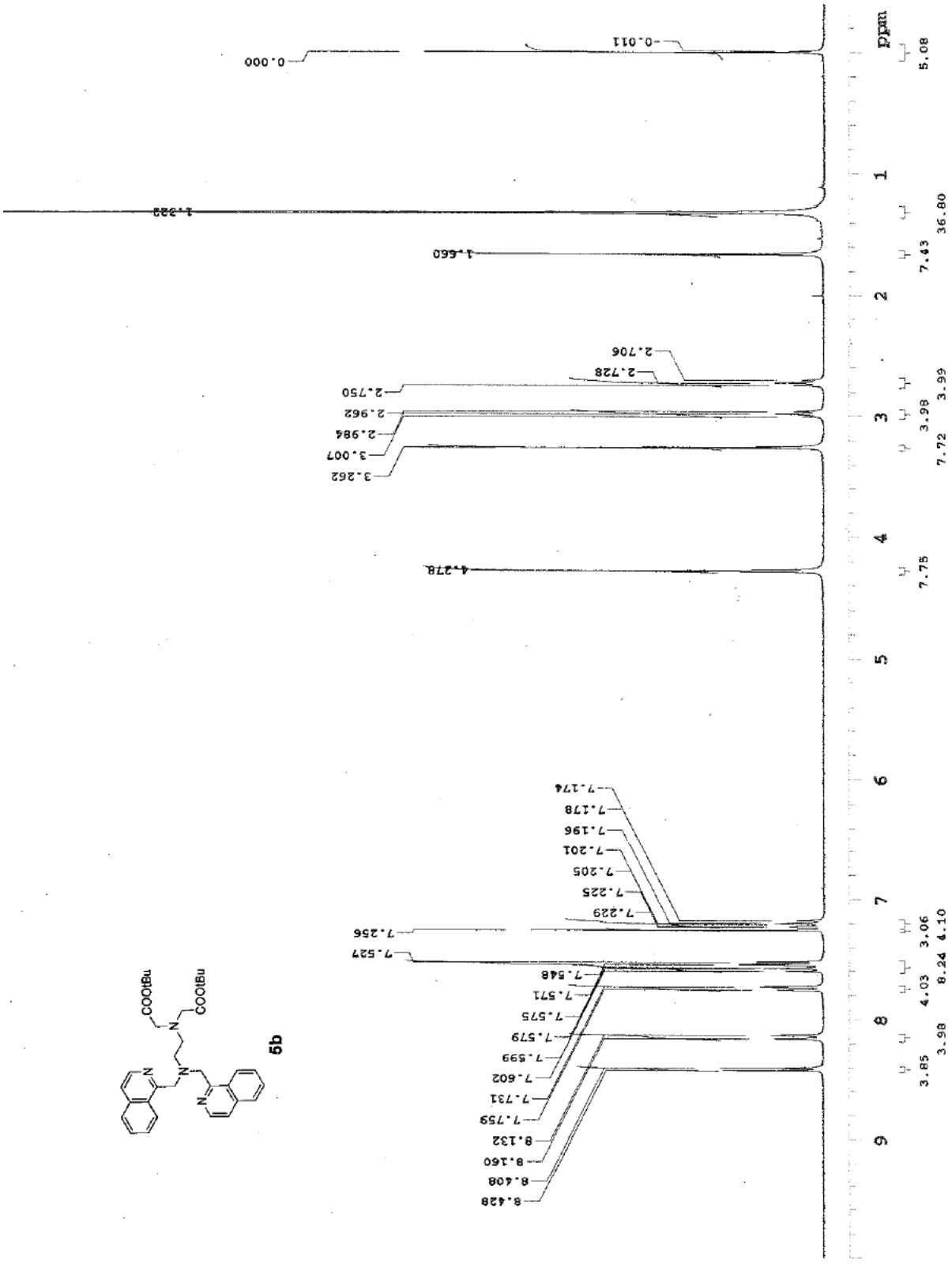


Fig. S26. ^{1}H NMR spectrum of **5b** in $CDCl_3$.

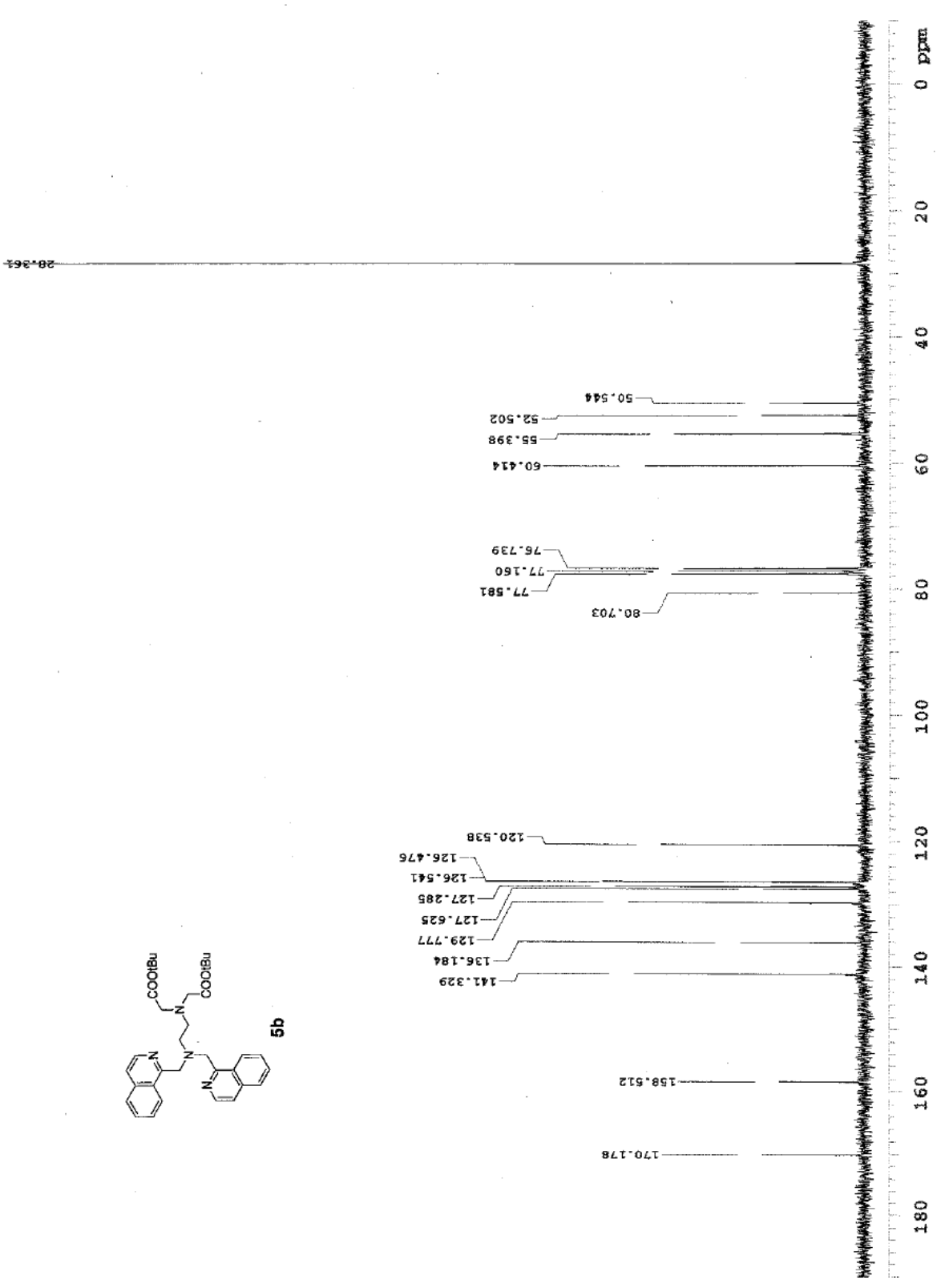


Fig. S27. ^{13}C NMR spectrum of **5b** in $CDCl_3$.

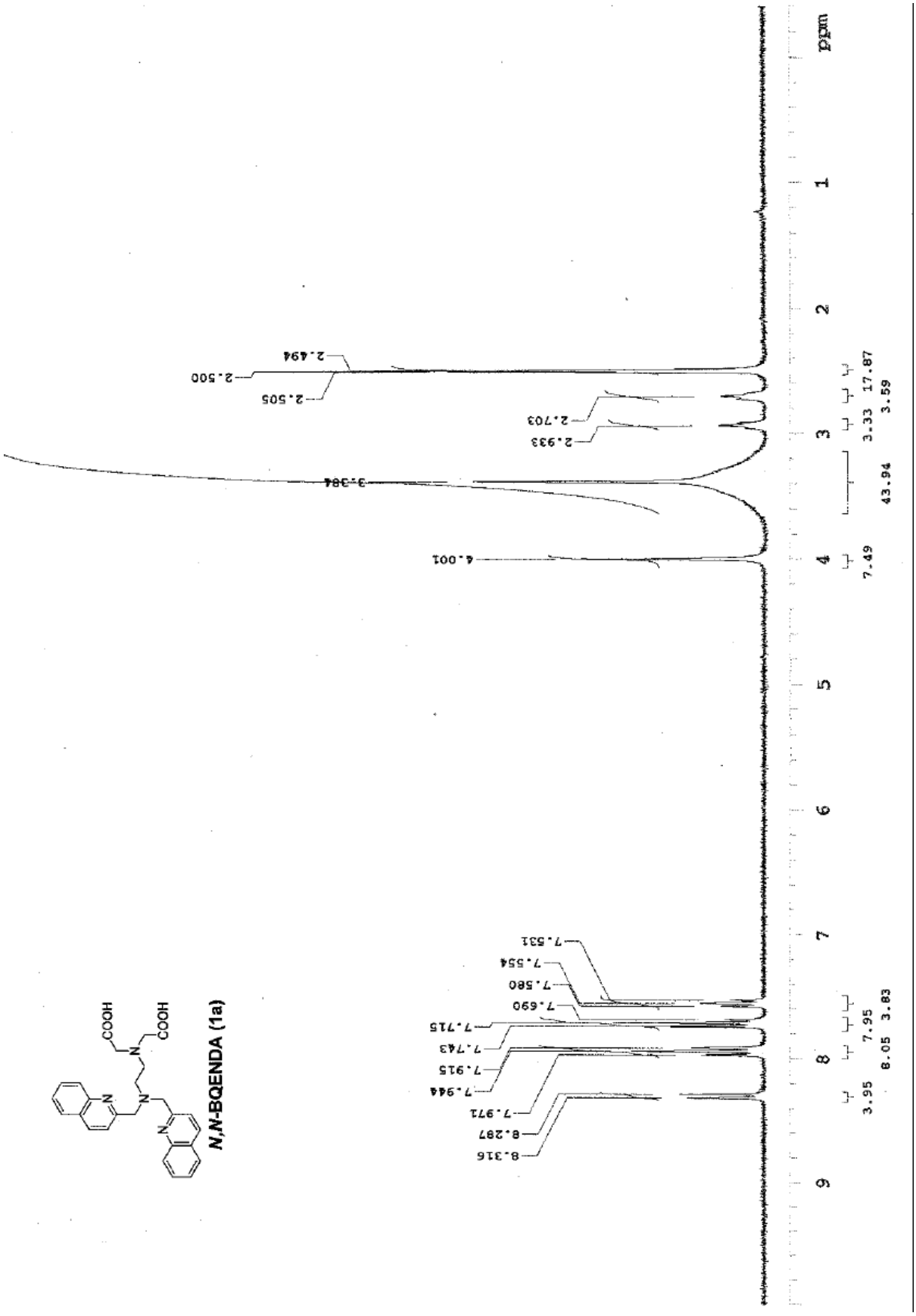


Fig. S28. ^{1}H NMR spectrum of **1a** in DMSO-d_6.

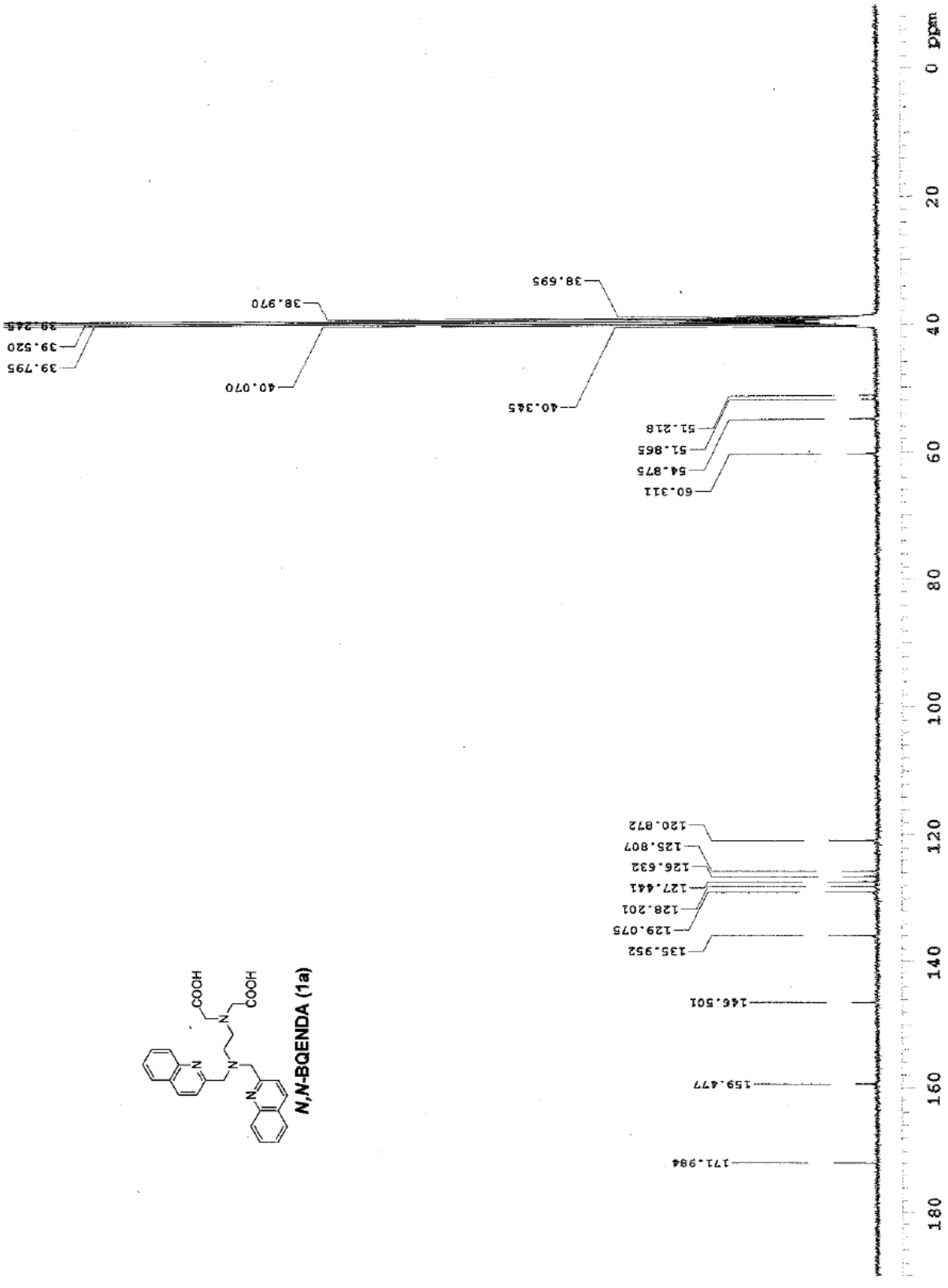


Fig. S29. ^{13}C NMR spectrum of **1a** in DMSO-d_6.

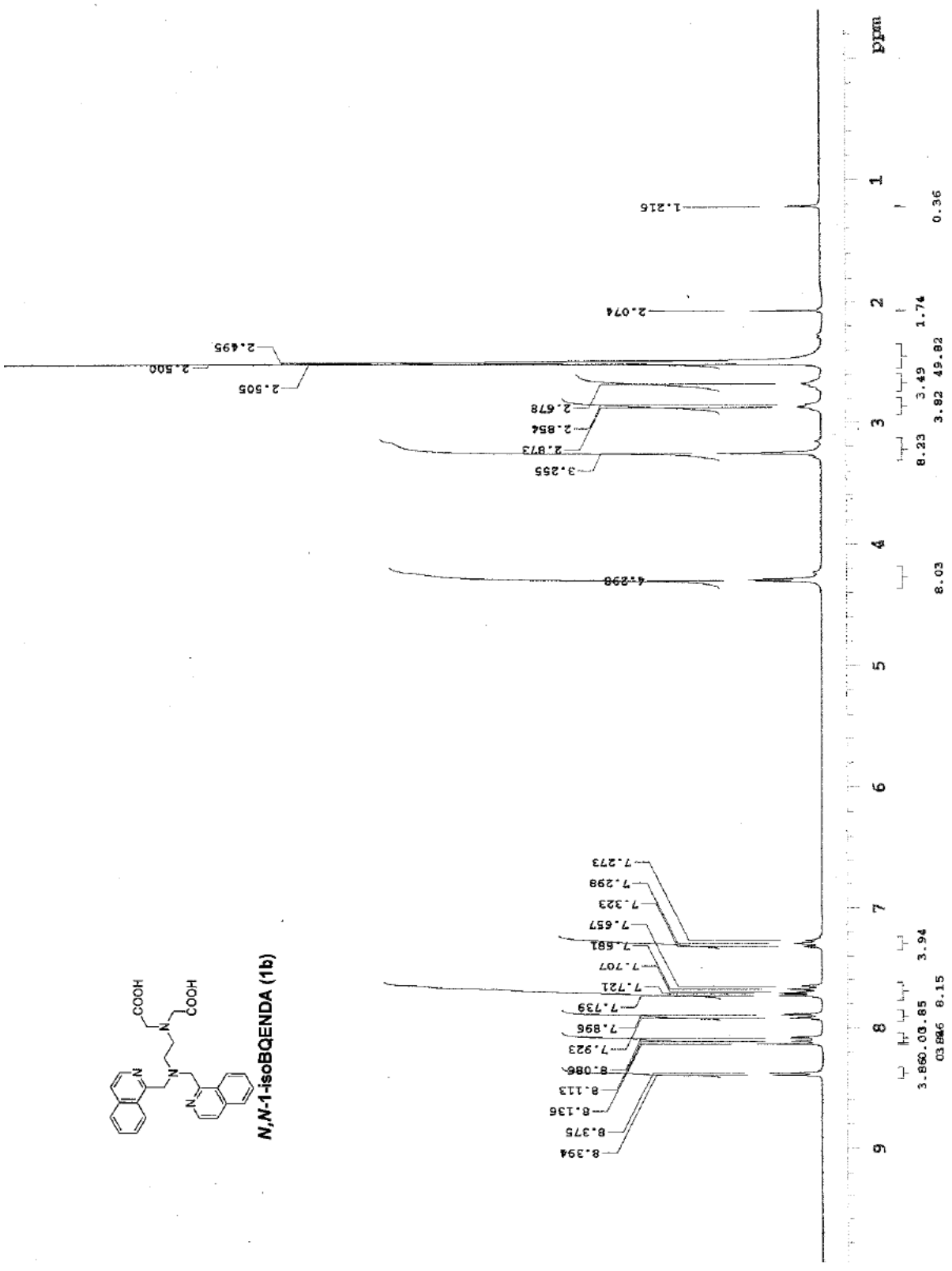


Fig. S30. ^{1}H NMR spectrum of **1b** in DMSO-d_6.

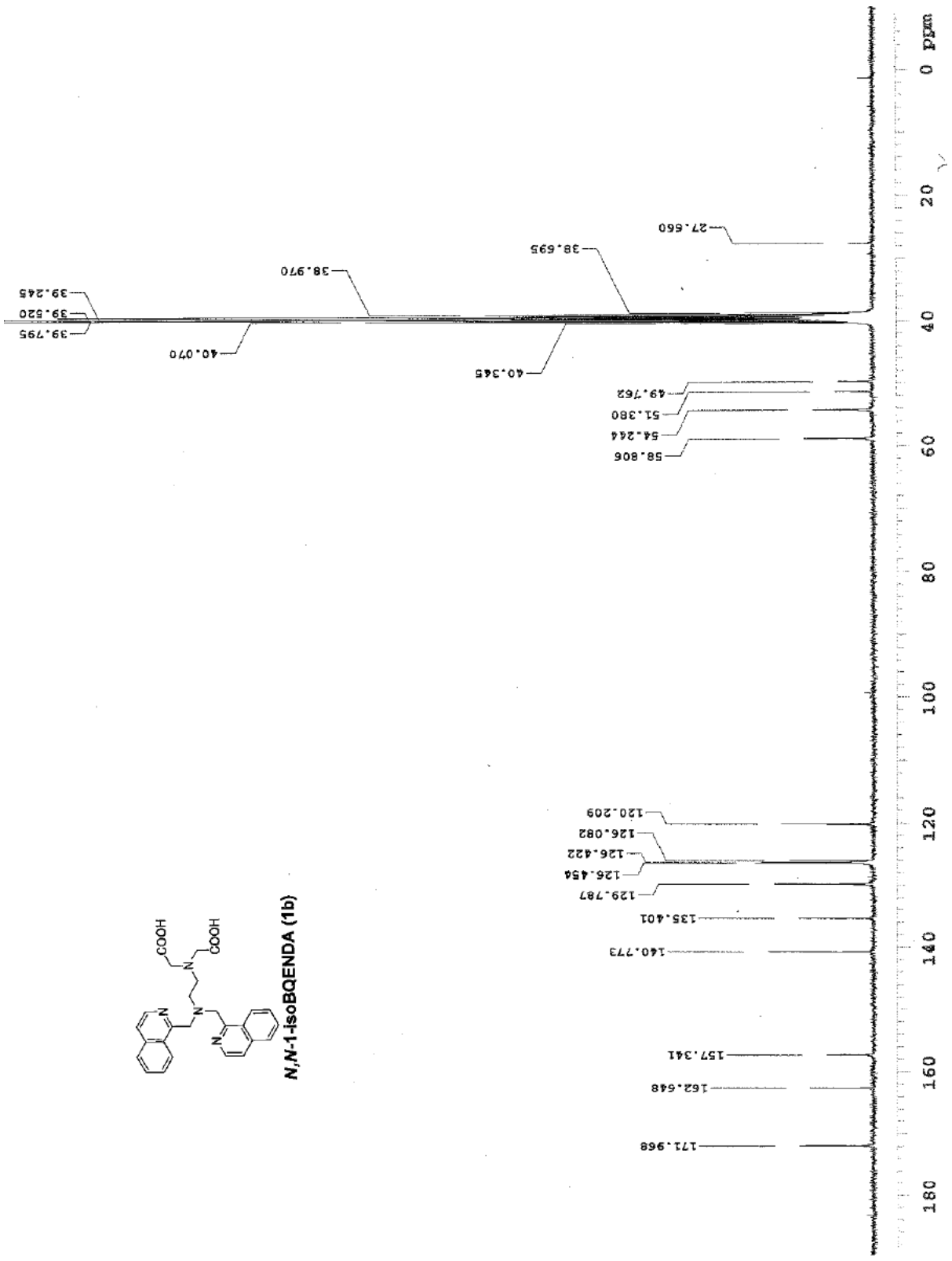


Fig. S31. ^{13}C NMR spectrum of **1b** in DMSO-d_6.

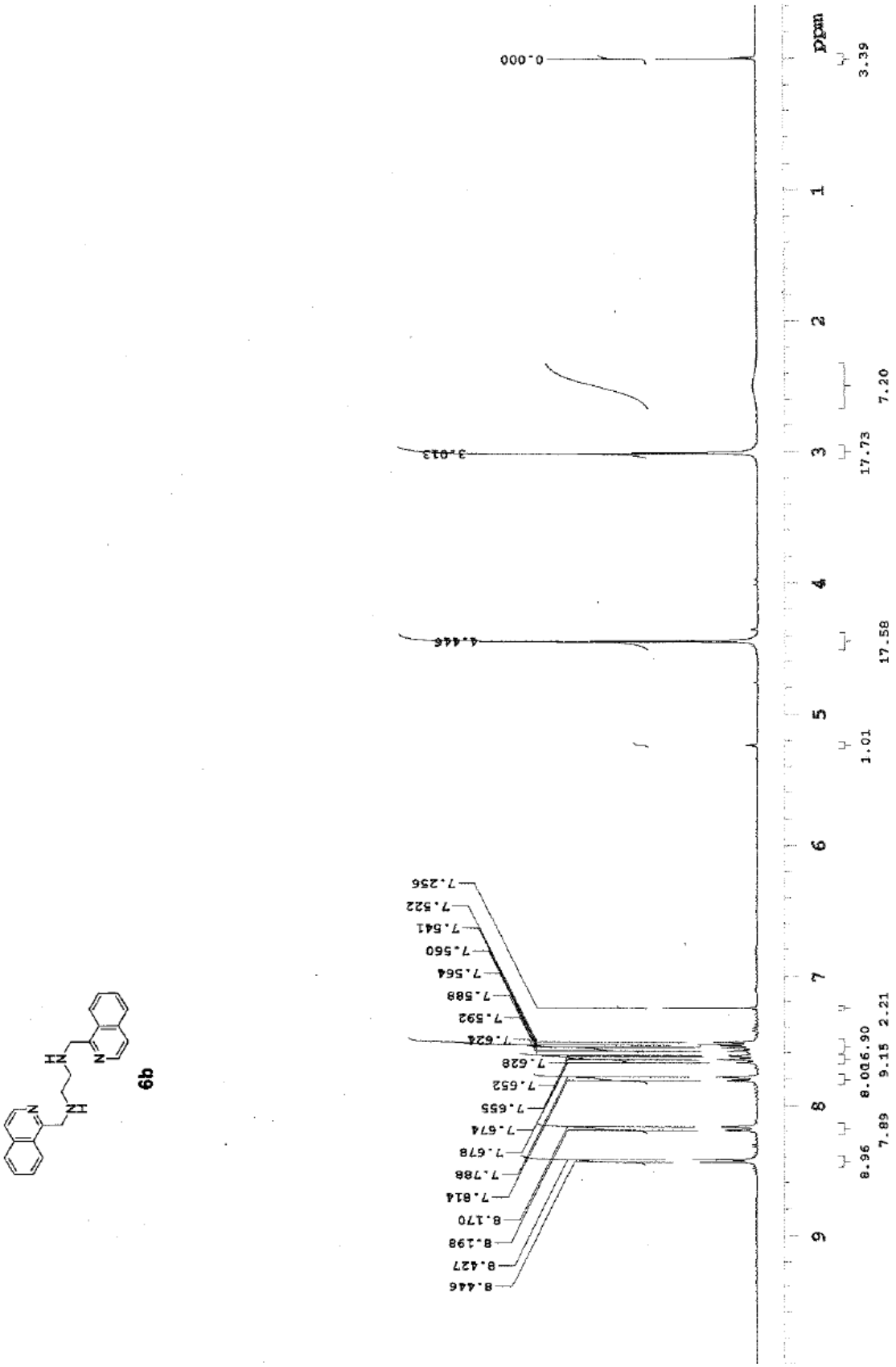


Fig. S32. ^{1}H NMR spectrum of **6b** in $CDCl_3$.

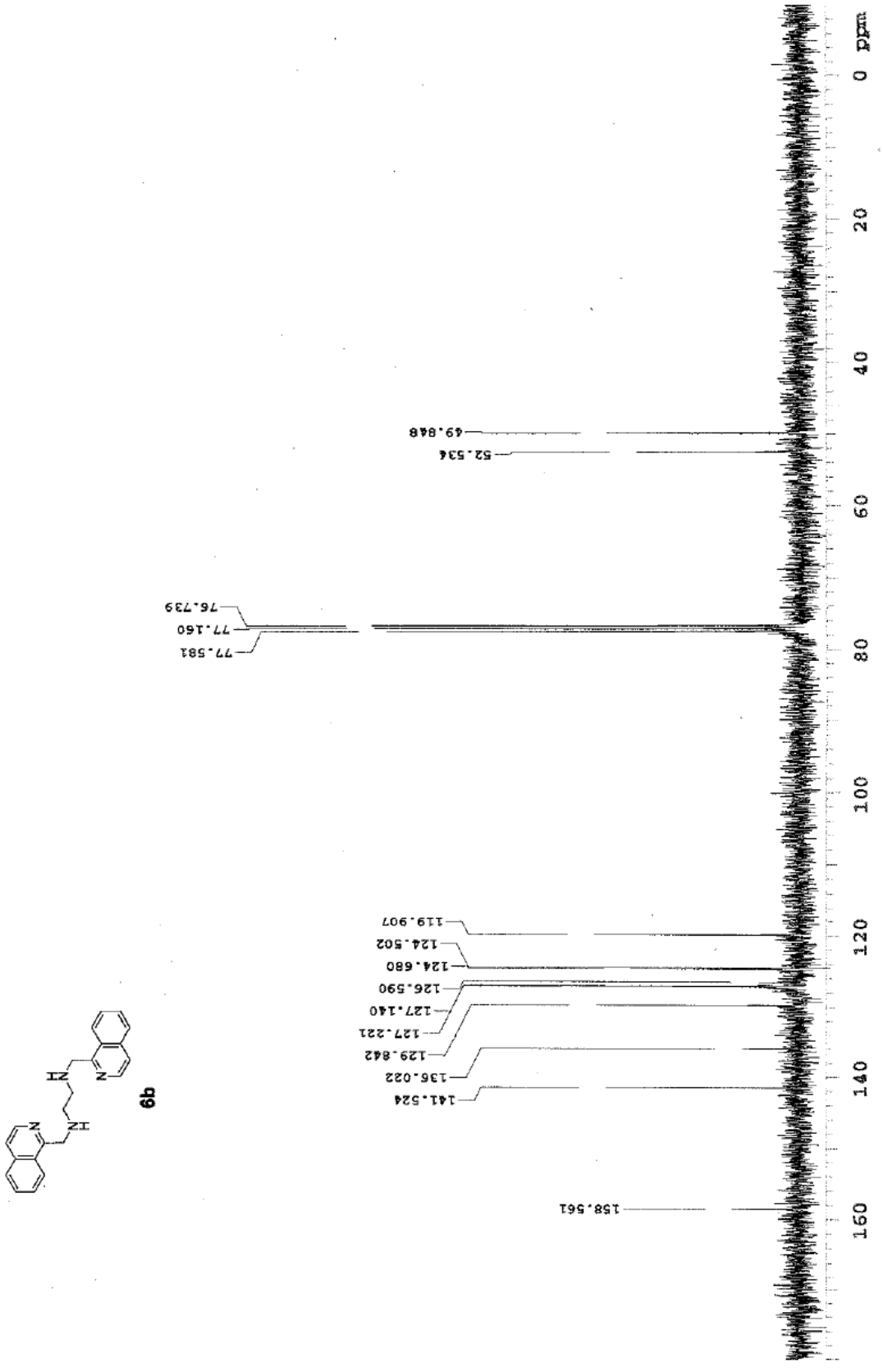


Fig. S33. ^{13}C NMR spectrum of **6b** in $CDCl_3$.

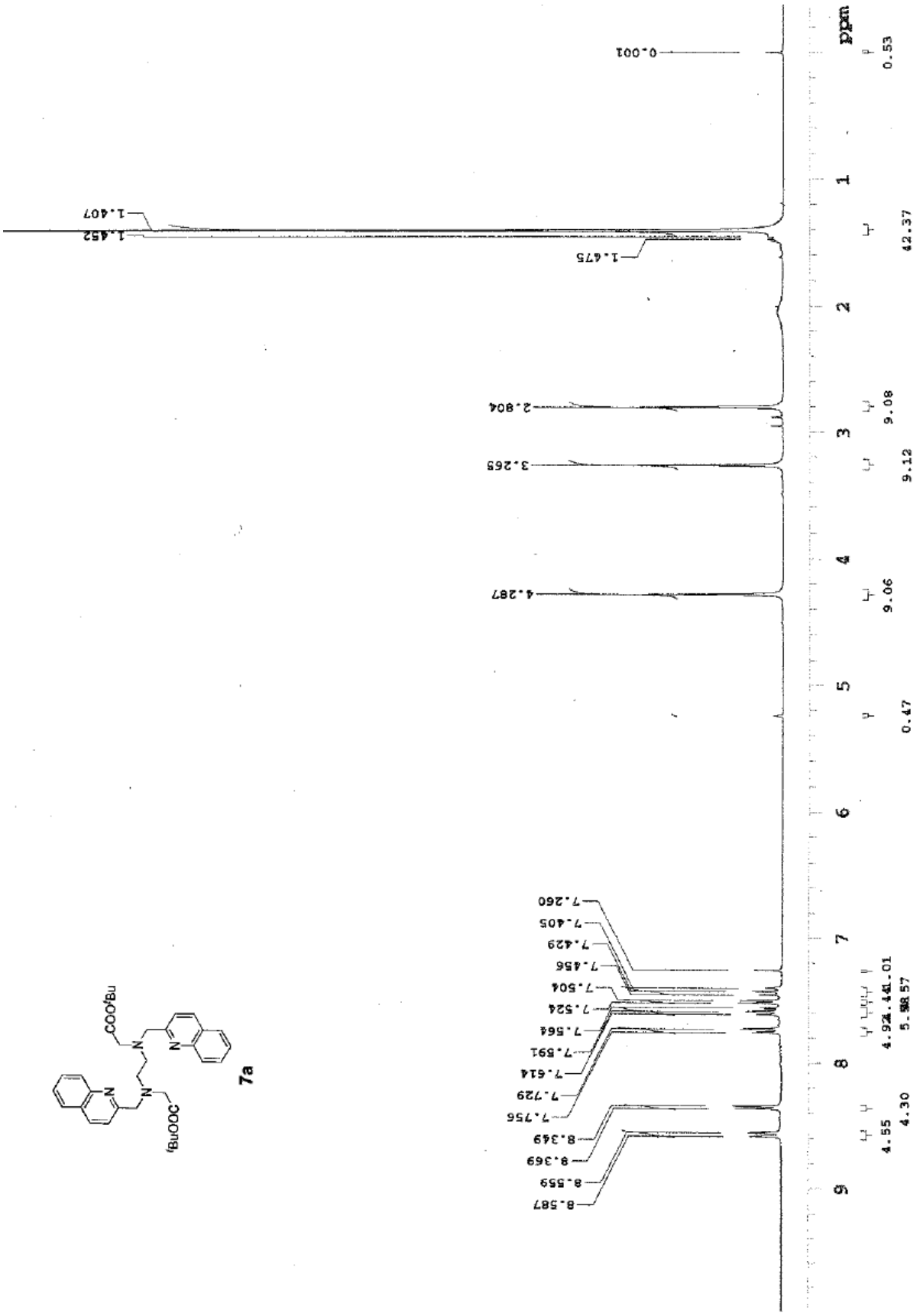


Fig. S34. ^{1}H NMR spectrum of **7a** in $CDCl_3$.

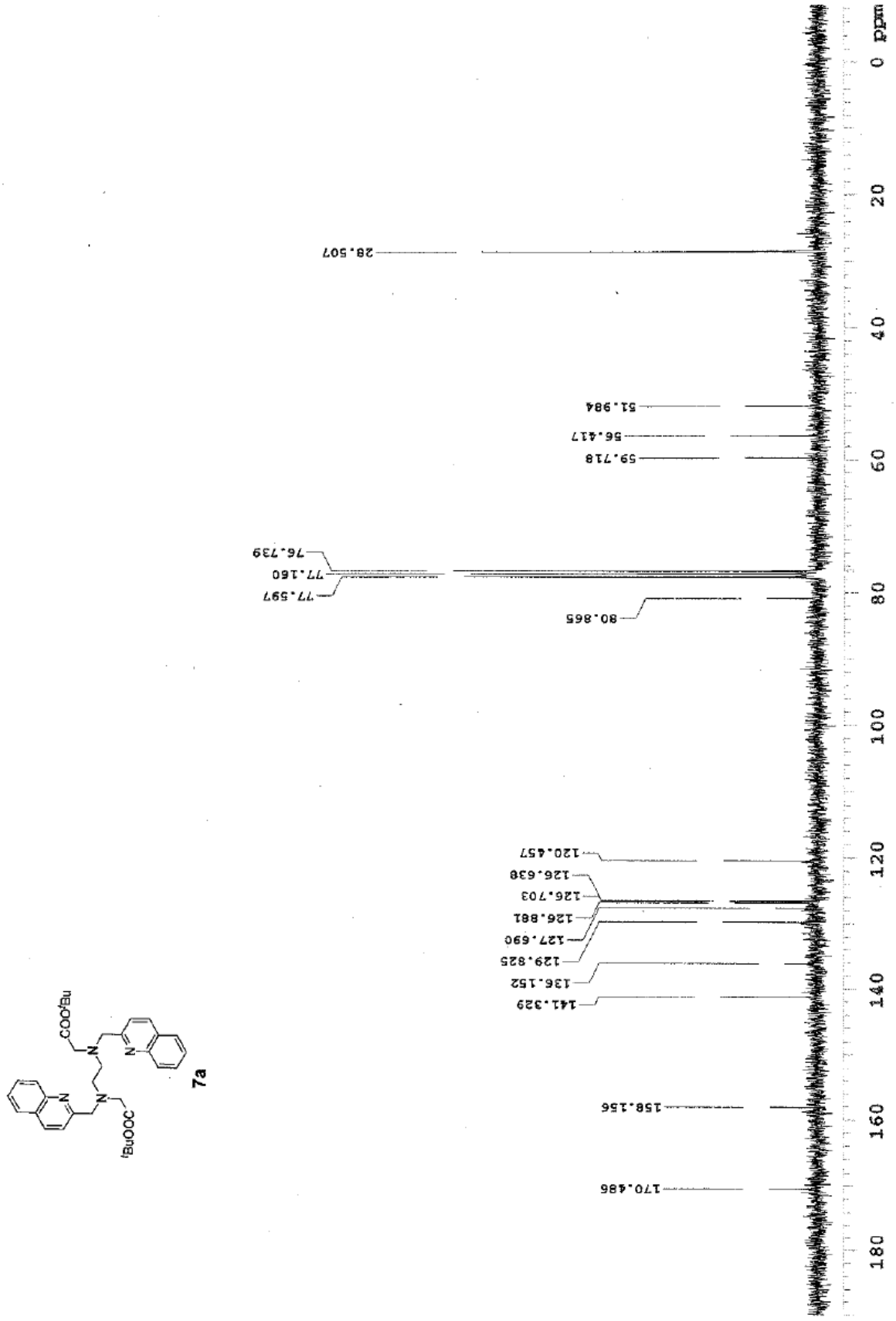


Fig. S35. ^{13}C NMR spectrum of **7a** in $CDCl_3$.

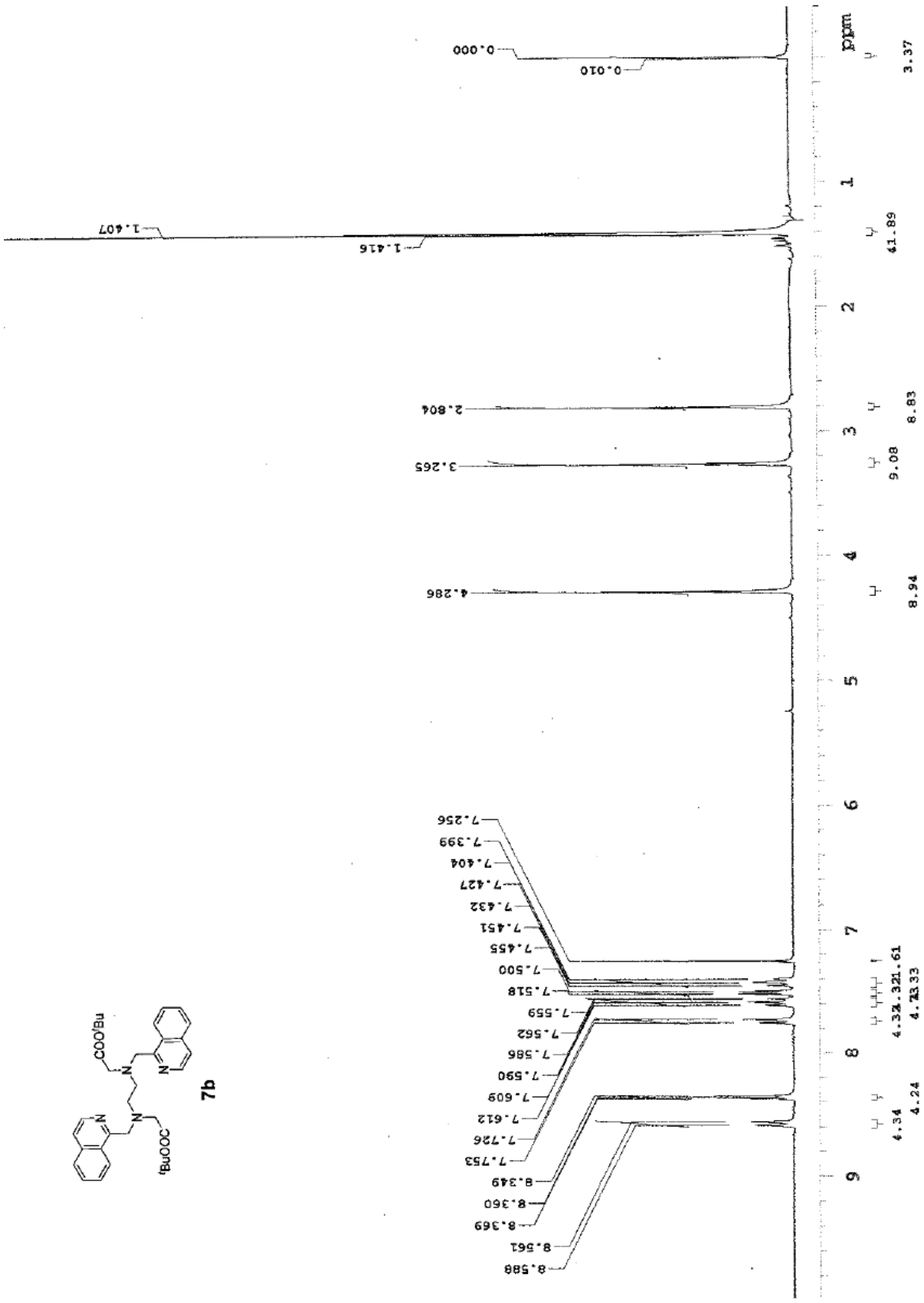


Fig. S36. ^{1}H NMR spectrum of **7b** in $CDCl_3$.

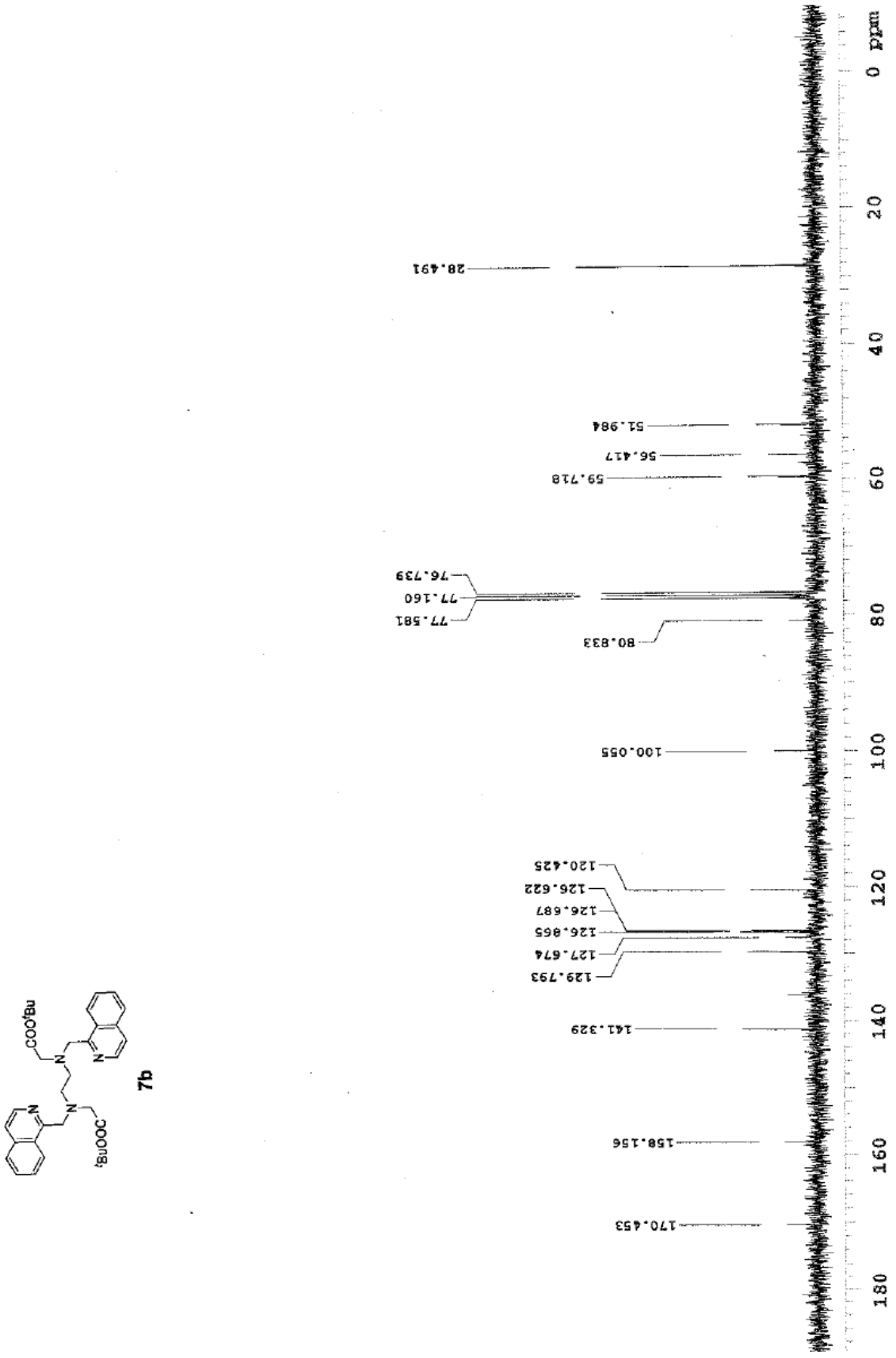


Fig. S37. ^{13}C NMR spectrum of **7b** in $CDCl_3$.

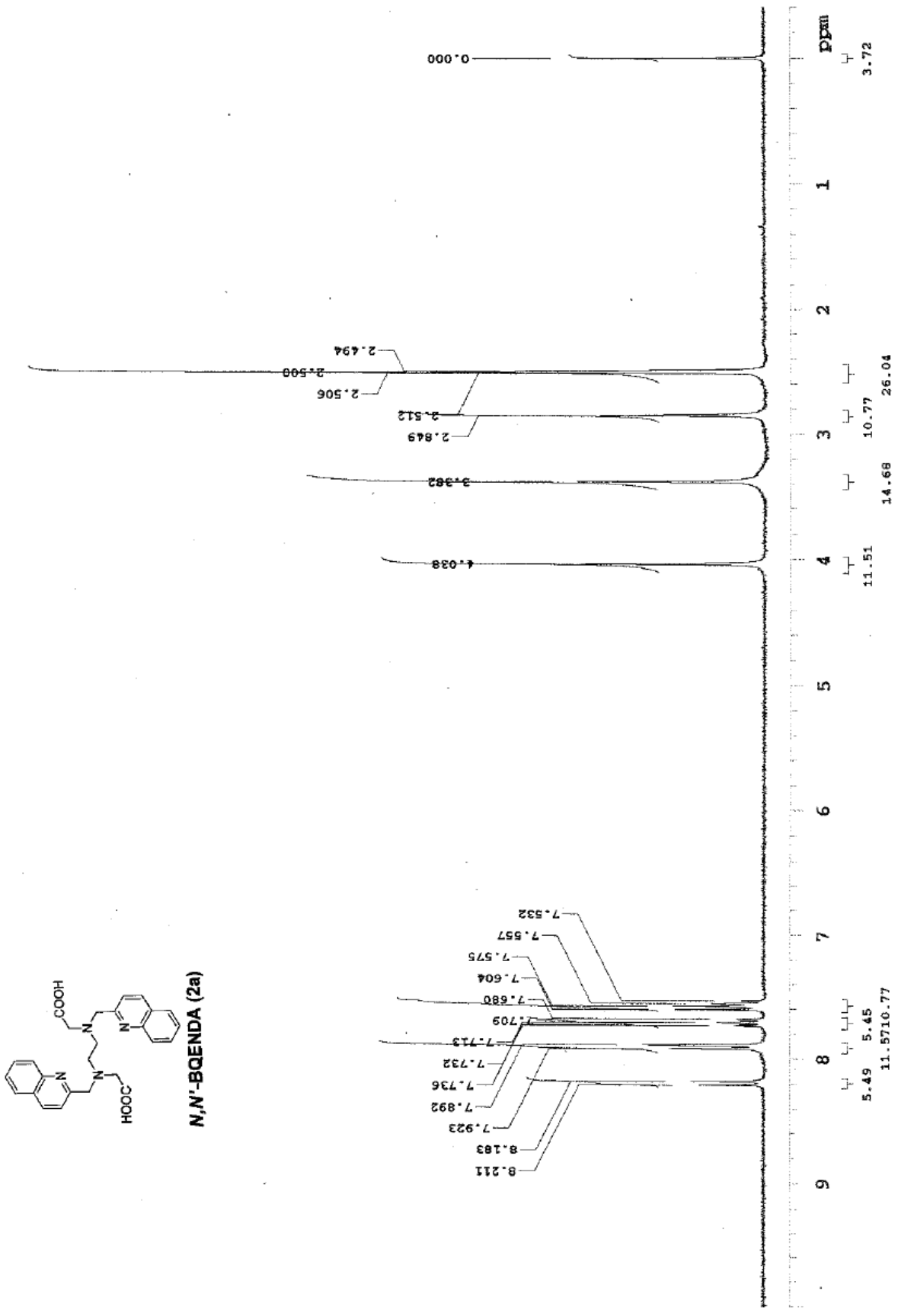


Fig. S38. ^{1}H NMR spectrum of **2a** in DMSO-d_6.

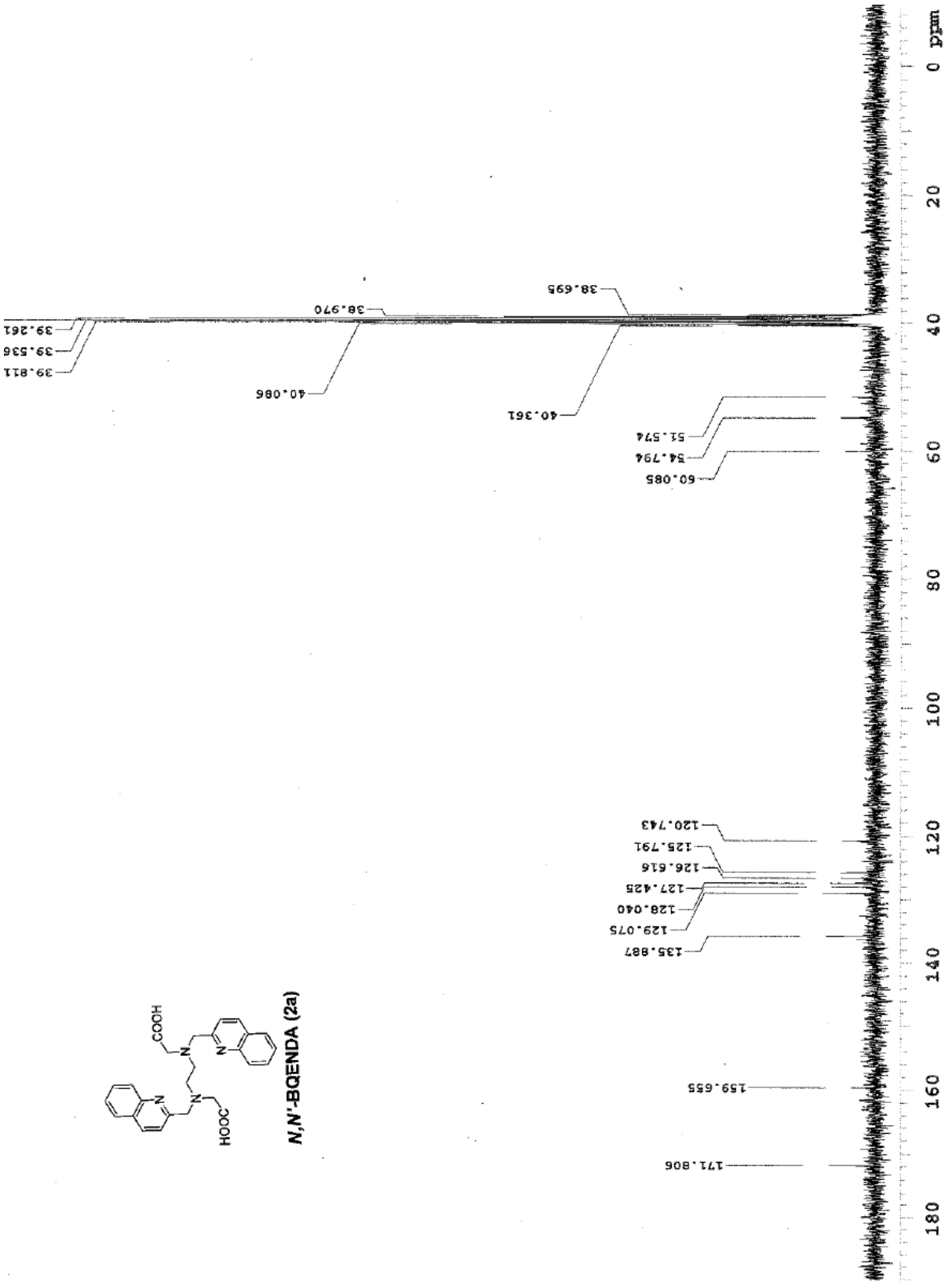


Fig. S39. ^{13}C NMR spectrum of **2a** in DMSO-d_6.

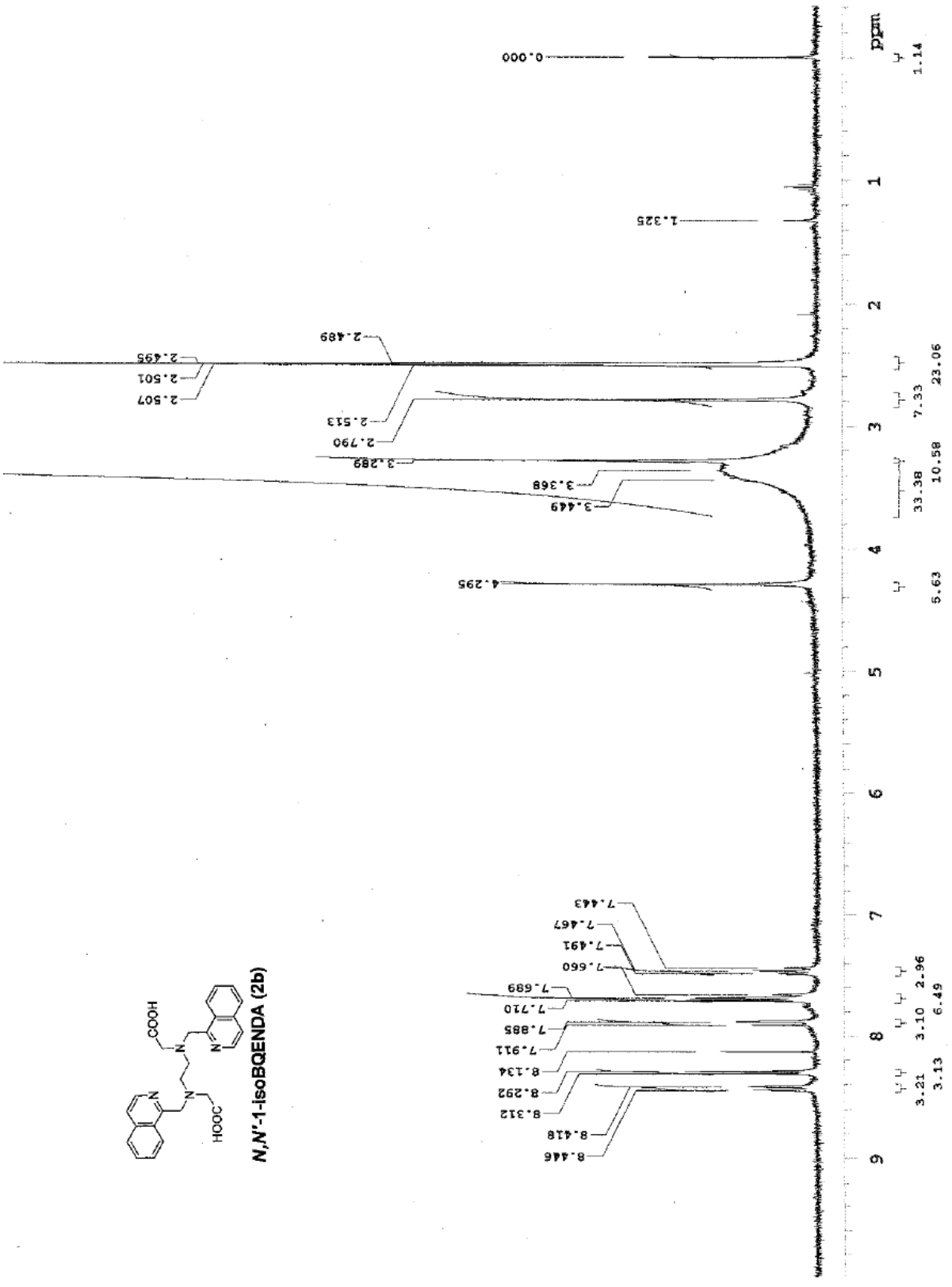


Fig. S40. ^{1}H NMR spectrum of **2b** in DMSO-d_6.

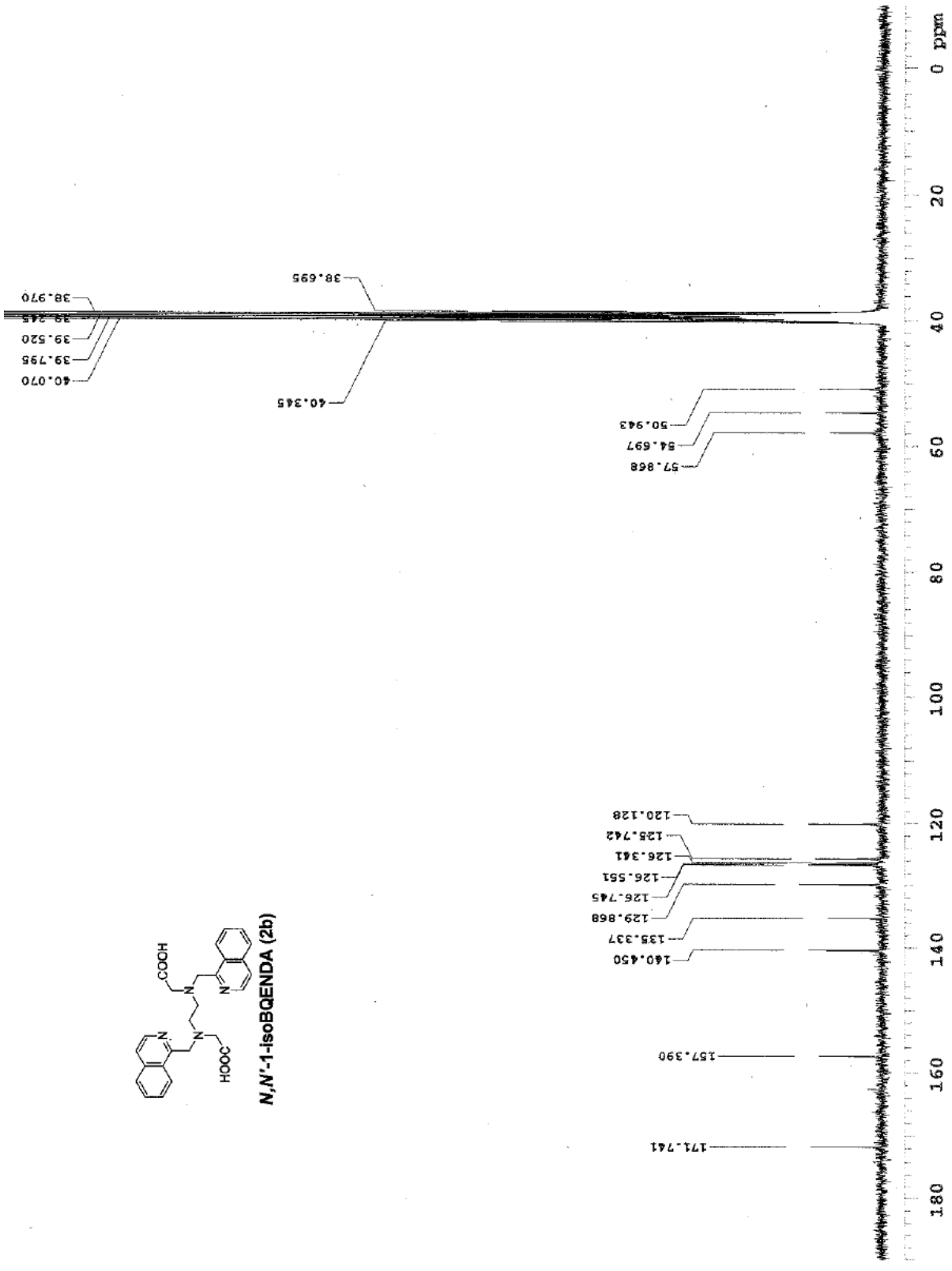


Fig. S41. ^{13}C NMR spectrum of **2b** in DMSO-d_6.

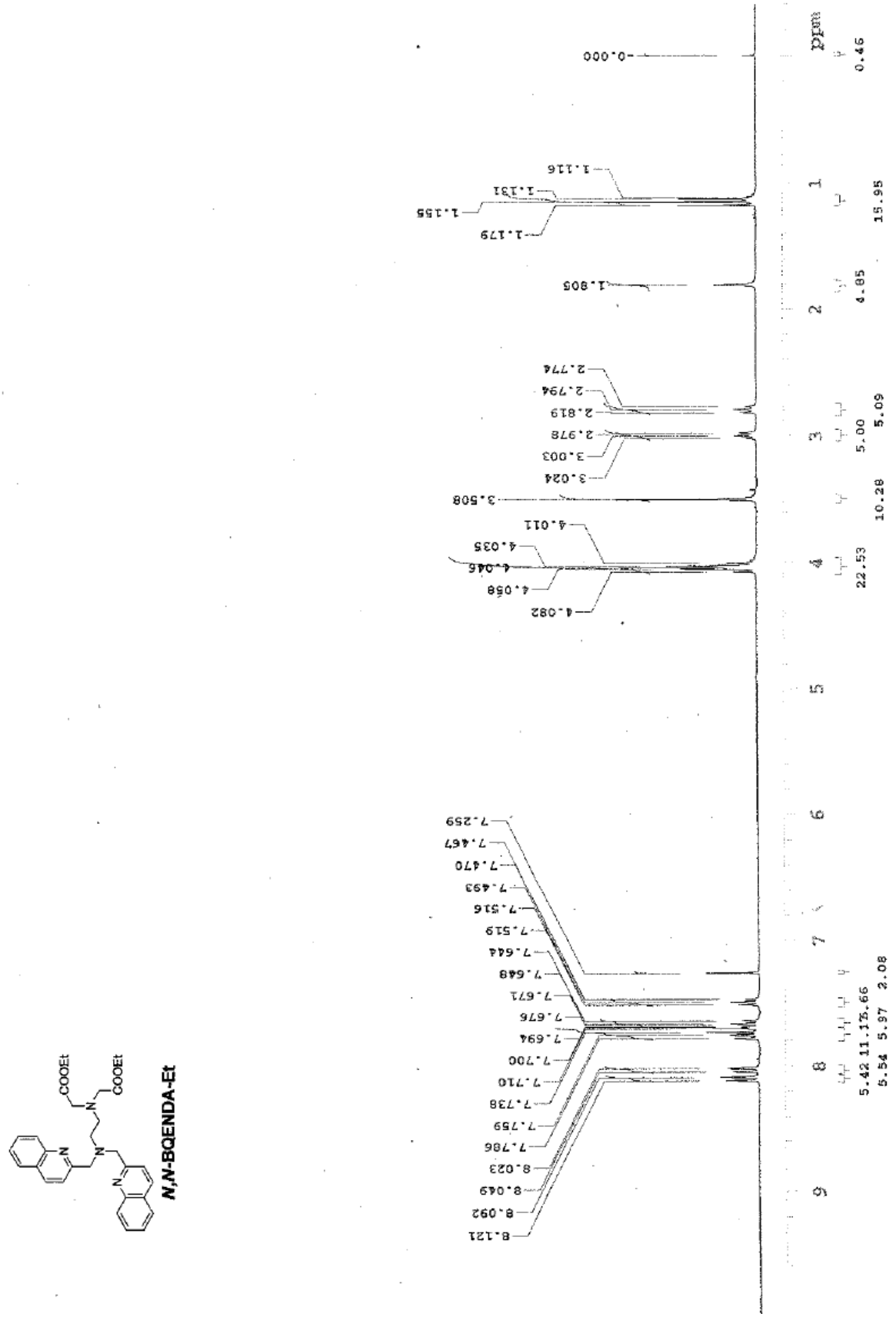


Fig. S42. ^{1}H NMR spectrum of *N,N*-BQENDA-Et in $CDCl_3$.

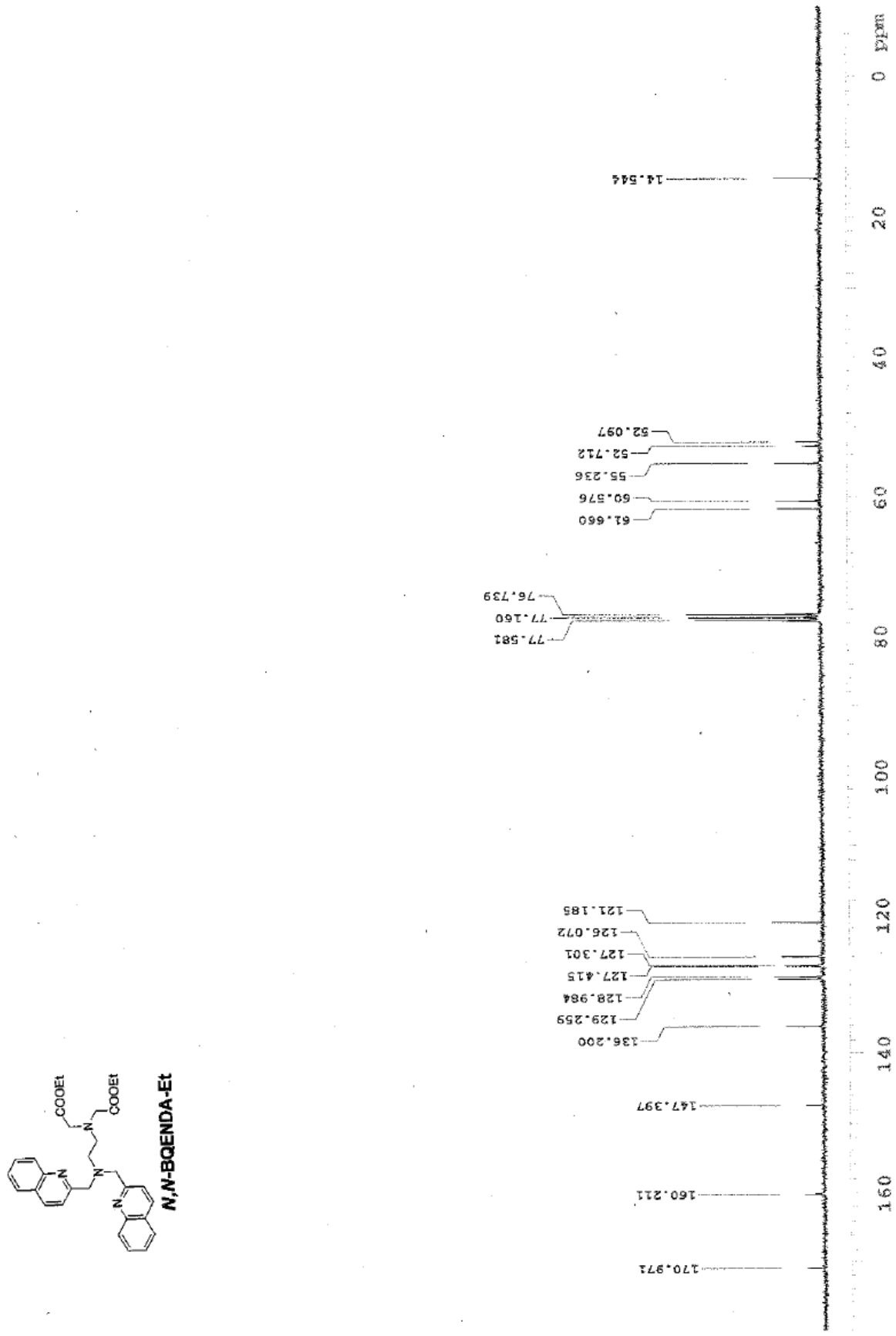


Fig. S43. ^{13}C NMR spectrum of *N,N*-BQENDA-Et in $CDCl_3$.

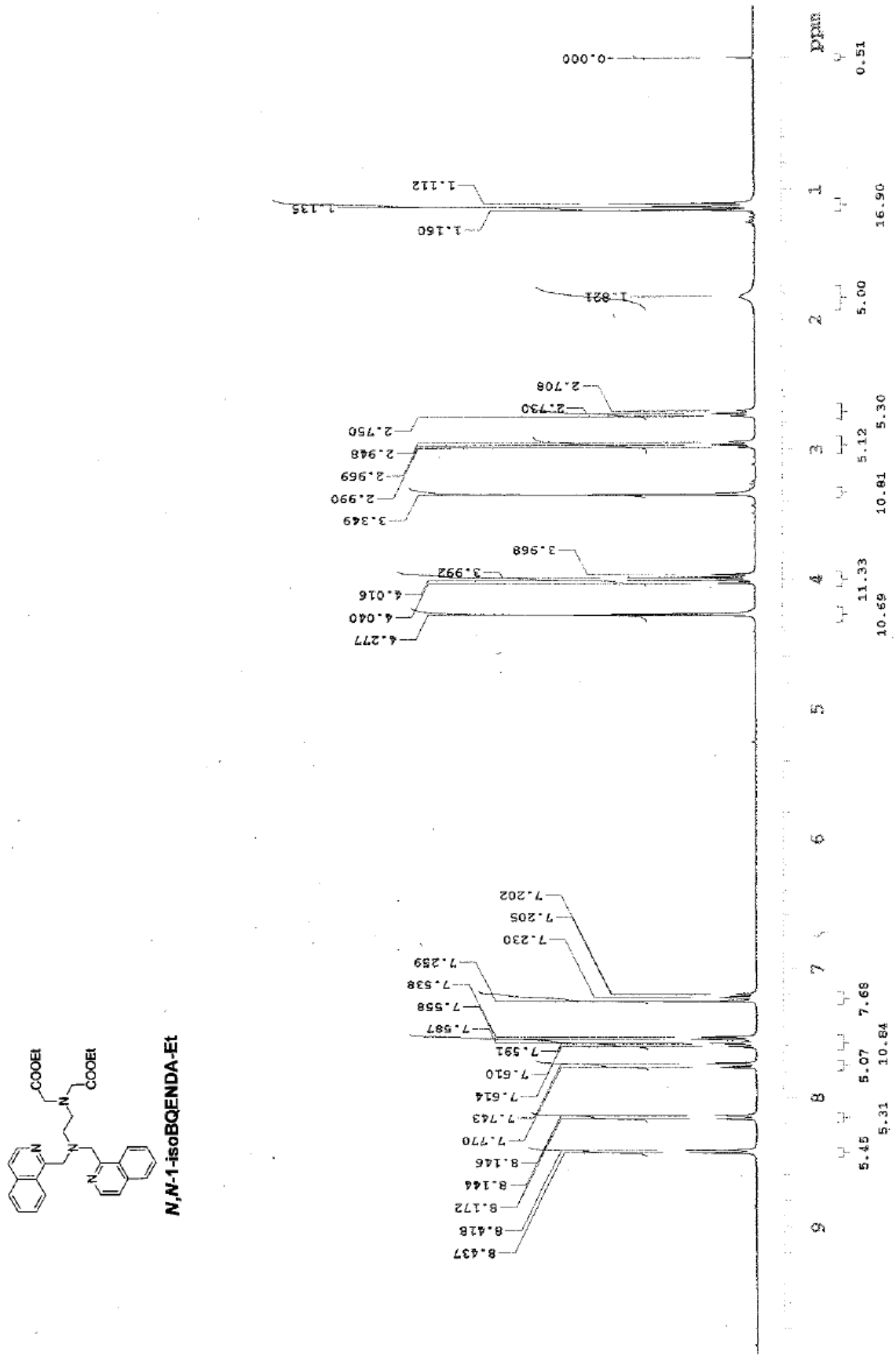


Fig. S44. ^{1}H NMR spectrum of *N,N*-1-isoBQENDA-Et in $CDCl_3$.

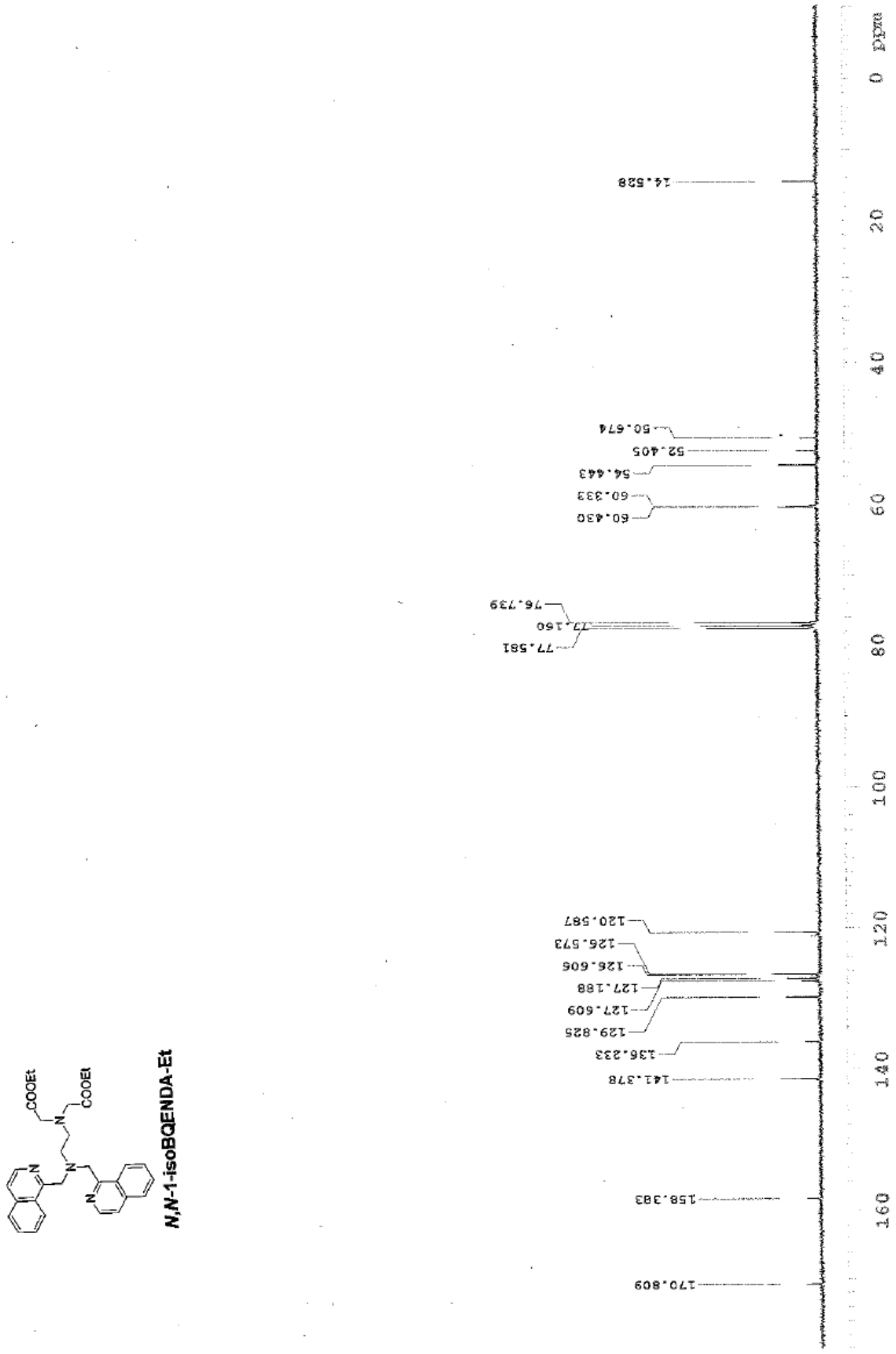


Fig. S45. ^{13}C NMR spectrum of *N,N*-1-isoBQENDA-Et in $CDCl_3$.